THE THERMOLYSIS OF gem-DIFLUOROSPIROPENTANE, THE KINETIC EFFECT OF FLUORINE ON THE HOMODIENYL HYDROGEN SHIFT, AND PREPARATION AND REACTIONS OF DIFLUORODIIODOMETHANE

By

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To Harvey and Joanne Hall
without whom this would not have been possible.

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An isotopic labeling experiment showed that 1,1-difluorospiropentane thermally rearranges to 2,2-difluoromethylenecyclobutane via two competing mechanisms which are analogous to the rearrangement of the parent hydrocarbon. One mechanism involves initial cleavage of the C_1-C_2 bond and the other involves initial C_4-C_5 bond cleavage. The former pathway predominates by 3 to 1. Difluorocarbene addition to (dideuteromethylene)cyclopropane gave 1,1-Dideutero-2,2-difluorospiropentane. Gas phase thermolysis at 339.6°C ($k = 2.363 \pm 0.025 \times 10^{-5} s^{-1}$) produced a mixture of the three possible gem-dideuterated isomers of 2,2-difluoromethylenecyclobutane.

The relative amounts of these were determined by ^{1}H and ^{19}F NMR spectroscopy. The small secondary isotope effect observed (k_H/k_D = 1.15±0.02) is consistent with the major reaction path involving initial C_1-C_2 bond homolysis.

Cis,cis-1-fluoro-2-methyl-3-vinylcyclopropane was prepared in 35% yield by treatment of cis-1,3-pentadiene with $CHFI_2$ and diethylzinc. Its gas phase thermolysis at 152.8 - 171.4°C produced a mixture of trans- and cis-1,3,5-hexatriene the latter of which equilibrated with 1,3-cylco-hexadiene under the reaction conditions. Rate constants for this first order, unimolecular process were measured at 6 temperatures and activation parameters were calculated (E_a=27.6±1.2 kcal/mol, Log A = 10.3±0.6). These results are consistent with an initial 1,5-homodienyl hydrogen shift followed by rapid HF elimination.

Treatment of 1,3-cycloheptadiene with $CHFI_2$ and diethyl-zinc afforded endo- and exo-8-fluorobicyclo[5.1.0]oct-2-ene. Gas phase thermolysis of either isomer produced an approximately 2:1 ratio of 1-fluoro- and 7-fluoro-1,3-cyclooctadiene. Some preliminary kinetic studies were carried out. Possible mechanisms which account for these unexpected products are presented.

Difluorodiiodomethane, which was previously available only in small amounts via difficult and low yield procedures, was prepared in practical quantities by treatment of CI_4

with HgF_2. As a difluorocarbene synthon, CF_2I_2 was used in photochemical and Simmons-Smith cyclopropanations. Free-radical additions of CF_2I_2 to alkenes gave α,α-difluoro-α,γ-diiodo adducts in good to excellent yields.

CHAPTER 1
GENERAL INTRODUCTION AND THEORY

Fluorine as a Substituent

Fluorine is unique among substituents in its effects on organic systems. The high electronegativity, unshared electron pairs, and small size of fluorine make it a potent σ-withdrawer and a potential π-donor while at the same time having minimum steric requirements. A brief description of these properties is presented here, but the interested reader is directed to the excellent reviews of Smart[1,2] for a more comprehensive treatment.

Electronegativity

Fluorine is the most electronegative of the elements. The electronegativity demands of fluorine result in a C-F bond that is rich in p-character as carbon gives up its less tightly held p electrons.[3] Fluorinated organic molecules often display changes in geometry reflecting changes in hybridization relative to their hydrocarbon analogues. Consider, for example, the enlarged HCH angle of 113.7° for CH_2F_2 [4] compared with the idealized 109.5° of CH_4.

Non-bonding Electrons

The presence of three non-bonded pairs of electrons on a fluorine make it a potential π-donating substituent. This property is nicely illustrated by the observations that fluorine directly bound to a carbocation center stabilizes the carbenium ion.[5] This is best explained as conjugative interaction of fluorine's lone pairs with the vacant p-orbital of the carbenium ion, (1).

(1)

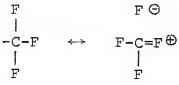
The π-donor capability of fluorine has also been used to explain the observed trends in bond dissociation energies of the halomethanes (Table 1-1).[6] Note that as halogen content increases, D°(C-X) decreases for iodo-, bromo- and chloromethanes. This trend is reversed for fluoromethanes and spans a wider range of energies.

Table 1-1. Bond Dissociation Energies, D°(C-X) of Halomethanes.[a]

X	CH_3X	CH_2X_2	CHX_3	CX_4
F	109.9±1	119.5[b]	127.5[b]	130.5±3
Cl	84.6±0.2	80.1	77.6	73.1±1.8
Br	70.9±0.3	64[c]	62[c]	56.2±1.8
I	57.2±0.3	51.3[c]	45.7[c]	-

[a]All data from ref. 7 unless otherwise noted.
[b]Ref. 8.
[c]Ref. 9.

Pauling[6] suggested that contributions from "double-bond, no-bond" resonance forms (2) account for these results. As n increases from 0 to 4 for $CH_{(4-n)}F_n$, a greater number of such forms can be drawn. Ab initio calculations seem to support this description.[10,11]



(2)

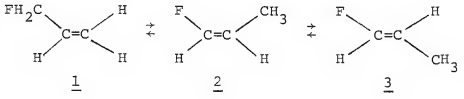
Size

With regard to fluorine's size, two points should be made. Excluding hydrogen, fluorine has the smallest

Van der Waals radius of any substituent atom or group.[12] This means that the steric requirements for a fluorine are minimal. Fluorine's small size also makes it well suited for overlap of its atomic orbitals with those of carbon. This results in a strong C-F bond. In fact, of all the elements, fluorine forms the strongest single bonds to carbon.

Fluorine as a Substituent on Alkenes

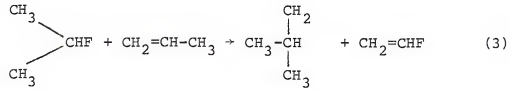
The effects of vinylic fluoro substituents have frequently been misunderstood and misrepresented. Contrary to what was once believed,[13] monofluoro and gem-difluoro substituents stabilize alkenes thermodynamically. The equilibration of fluoropropenes shows that a single fluorine is thermodynamically favored on the C=C bond by about 3 kcal/mol.[14]



1 2 3

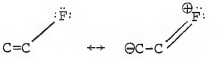
	ΔH_r, kcal/mol
1 → 2	-3.34
1 → 3	-2.68
2 → 3	+0.64

Equation (3), which is useful for calculating substituent effects relative to CH_3,[15] seems to indicate that F is similar to CH_3 in its ability to stabilize a double bond. A CH_3 is considered to stabilize a C=C bond by about 3 kcal/mole.[16]



$$\Delta H_r = 0.0 \pm 1.0 \text{ kcal/mole}$$

The increased thermodynamic stability of monofluoro olefins is most easily explained by the resonance contribution depicted in equation (4) in which the non-bonding electrons of fluorine back-bond into the CC_π bond. This description is supported by ab initio calculations.[11,17,18]



(4)

Geminal difluoro substitution on a C=C bond is also thermodynamically stabilizing. The π-bond dissociation energies[19] for ethylene, gem-difluoroethylene, and tetrafluoroethylene are shown in Table 1-2.

Table 1-2. π-Bond Dissociation Energies.

	D°_{π} kcal/mol
$CH_2=CH_2$	59.1 ± 2.0[a]
$CH_2=CF_2$	62.1 ± 1.0[b]
$CF_2=CF_2$	52.3 ± 2.0[c]

[a]Ref. 19.
[b]Ref. 20.
[c]Ref. 21.

It appears that the π-bond of $CH_2=CF_2$ is stabilized relative to $CH_2=CH_2$ and to $CF_2=CF_2$. Consider also the ΔH_r for the isodesmic reaction (5).

$$CF_2=CF_2 + CH_2=CH_2 \rightarrow 2\ CH_2=CF_2 \qquad (5)$$
$$\Delta H_r = -14.6 \text{ kcal/mol}$$

$$D^{\circ}_{\pi}(CF_2=CF_2) + D^{\circ}_{\pi}(CH_2=CH_2) - 2D^{\circ}_{\pi}(CH_2=CF_2) = \qquad (6)$$
$$-14.2 \text{ kcal/mol}$$

The similarity in the value of equation (6) to the ΔH_r of equation (5) implies that the thermodynamic stability of $CH_2=CF_2$ relative to $CH_2=CH_2$ and $CF_2=CF_2$ is due almost entirely to stabilization of the π-bond.

At first these conclusions may seem inconsistent with some of the thermodynamic studies of gem-difluoro systems. The Cope rearrangement of 4 to 5 (equation (7)), for example,

has a ΔH_r of -5.1±0.6 kcal/mol, and the heat of hydrogenation of gem-difluoroethylene is 6.2 kcal/mol more exothermic than that of ethylene (equations (8) and (9)).

		ΔH_4, kcal/mol	
		-5.1 ± 0.6[14]	(7)
4	5		

$$CH_2{=}H_2 + H_2 \rightarrow CH_3CH_3 \qquad -32.6\pm0.3^{2} \qquad (8)$$

$$CH_2{=}CF_2 + H_2 \rightarrow CH_3CHF_2 \qquad -38.8\pm2.8^{2} \qquad (9)$$

These observations are not, however, a result of the destabilization of the alkene, but rather, a strong stabilization of the allylic and alkylic positions by gem-difluoro substitution. A useful concept here is that of "Incremental geminal stabilization"[14] (IGSTAB) which is defined as the increase in thermodynamic stabilization of a geminally substituted system, per substituent, relative to the respective monosubstituted system. Isodesmic equations are used to determine these quantities and, as shown below, IGSTAB values are strongly system-dependent.

	ΔH_r, kcal/mol		IGSTAB, kcal/mol	
$2CH_3CH_2F$	13.1	$CH_3CHF_2 + CH_3CH_3$	-6.6	(10)
$2CH_2=CHF$	-5.0	$CH_2=CF_2 + CH_2=CH_2$	-2.5	(11)
$2CH_2=CHCH_2F$	-13.25	$CH_2=CH_2CHF_2 + CH_2=CH-CH_3$	-6.6	(12)

Notice that the IGSTAB for the alkene is negative but those of the alkyl and allyl systems are even more negative. The driving force to convert vinyl CF_2 to alkyl or allyl is the greater stability of the latter two groups, i.e. larger IGSTAB, and not destabilization of the gem-difluoro olefins.

The difference in vinylic and alkylic IGSTAB has been rationalized using the double-bond, no-bond resonance model.[14]

6a ↔ 6b

7a ↔ 7b

A resonance contributor such as 6b would be expected to provide greater stabilization to 6 than 7b can for 7.* Analogous contributing structures cannot be drawn for the monofluoro alkyl and vinyl systems.

Fluorine as a Substituent on Cyclopropane

The advantages of cyclopropane ring systems for the study of substituent effects are well known.[22] How might the presence of fluorine substituents influence a cyclorpropane?

σ-Withdrawing effects

Consider first the inductive effects. The high electronegativity of fluorine causes its bonds to carbon to be rich in p-character and leaves the remaining bonds poorer in p-character.[3] This should result in an increased ring strain** as the unfluorinated sites are rehybridized to larger bond angles.

This description is neatly consistent with the observations for gem-difluorocyclopropanes. The structure of 1,1-difluorocyclopropane (Table 1-3) has been determined by microwave studies[24] and shows the C(1)-C(2) bond lengths to be shorter and the C(2)-C(3) bond length to be longer than the bonds of the parent cyclopropane.[25] One way to

* It may be helpful to recognize that the bonded portions of 6b and 7b are isoelectronic with a ketone and a ketene respectively.

** For purposes of this discussion the term "strain" is used to denote the total net destabilization. The reader is reminded that this may have several components.[23]

visualize this effect is to recognize that the "bent" bonds of the cyclopropane ring are even more bent with gem-difluoro substitution on carbon.[26] One would predict a qualitatively similar result, although smaller, for fluorocyclopropane (Table 1-3). The structure of $C\text{-}C_3H_5F$ is not known experimentally but has been calculated.[27]

Table 1-3. Bond Lengths.

	r[C(1)-C(2)], Å	r[C(2)-C(3)], Å
	1.510[a]	1.510[a]
	1.494-1.497[b]	1.527-1.528[b]
	1.464[c]	1.533[c]

[a]Ref. 25.
[b]Ref. 27.
[c]Ref. 24.

As has been noted elsewhere,[1,22,23] bond lengths cannot necessarily be correlated with bond strengths. Kinetic studies of gem-difluorocyclopropanes[22,28,29] indicate a general weakening of the C-C bonds compared to the corresponding hydrocarbons. Homolysis of the C(1)-C(2) bond is enhanced by 0 to 2 kcal/mol while C(2)-C(3) cleavage is enhanced by 8 to 10 kcal/mol.

There are currently no reports in the literature of a single fluorine's kinetic effect on cyclopropane opening.

π-Donating effects

A description of π-acceptor influence on cyclopropane was offered by Hoffmann[30] and extended by Günther[31] to include π-donors such as fluorine. Here one employs the familiar Walsh[32] model of cyclopropane bonding in which the carbons are sp^2 hybridized. One of the sp^2 hybrid orbitals from each carbon is directed into the ring and the remaining two are used to form σ-bonds to the hydrogens. The remaining p-orbitals, which are perpendicular to the CH_2 planes, overlap to form the "bent" C-C bonds. The Walsh molecular orbitals of the ring can be qualitatively represented as shown on the left of Figure 1-1.

In order to assess the effect of π-donors on this model, one considers the HOMO and LUMO of the interacting fragments. The LUMO of the cyclopropane is ψ_4 and the HOMO of a fluorine fragment is one of its three degenerate non-bonding atomic orbitals. As the fluorine donates electron density to the cyclopropane, the antibonding interactions for all C-C bonds increases. The implication here is that π-donors should destabilize the cyclopropane ring and weaken all the ring bonds.

Consistent with this model's inability to account for the observed shorter C(1)-C(2) bond lengths in 1,1-difluorocyclopropane is the recent report from Clark et al.[33] in

which they challenge the assumptions upon which the above model is based. These authors conclude that the σ-withdrawing effect of a fluorine far exceeds its π-donor capability in cyclopropane systems.

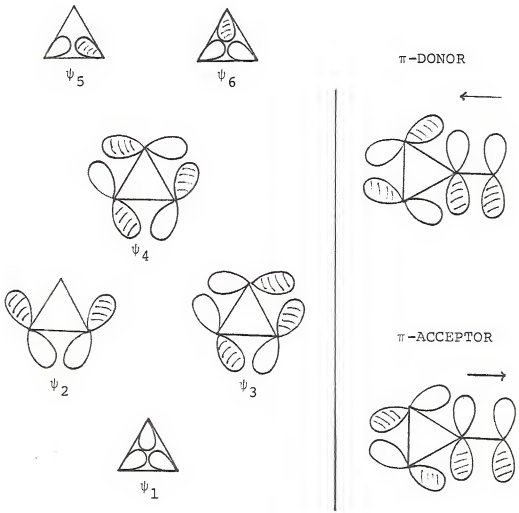
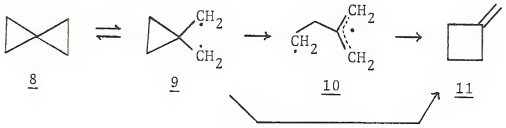


Figure 1-1. The Effect of π-Donors and π-Acceptors on the Walsh Orbitals of Cyclopropane.

CHAPTER 2
THERMOLYSIS OF 1,1-DIDEUTERO-2,2-DIFLUOROSPIROPENTANE

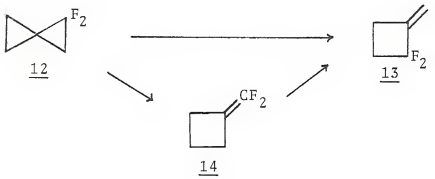
Introduction

Thermolyses of spiropentane systems have been studied extensively and the mechanism for the rearrangement of the parent hydrocarbon 8 is well understood. Initial cleavage of a peripheral bond[34] occurs reversibly[35] to produce diradical 9. Whether 9 then undergoes a second cleavage to give diradical 10 or goes directly to methylenecyclobutane 11 is not completely clear, but 11 has been shown to automerize via 10.[36] Activation parameters for the rearrangement of 8 to 11 have been determined.[37]



8 9 10 11

In order to further investigate the kinetic effects of gem-difluoro substitution in cyclopropane systems, 1,1-difluorospiropentane, 12, was studied by Dolbier et al.[38] Thermolysis of 12 gave 2,2-difluoromethylenecyclobutane 13 as the only product. Control experiments demonstrated that 10.5% of the observed product 13 was formed via (difluoromethylene)cyclobutane 14 which rapidly isomerized to 13 under the reaction conditions.



Activation parameters for the thermolysis of 12 are listed in Table 2-1 along with those for the parent hydrocarbon.

Table 2-1. Activation Parameters for the Thermolysis of Spiropentane and 1,1-Difluorospiropentane.

		E_a, kcal/mol	Log A	K_{rel} (340°C)
8		57.6±0.6	15.9±0.04	1.00
12		58.0±0.5	16.1±0.2	1.14

The modest rate enhancement of 12 relative to 8 (E_a and Log A equal within the experimental uncertainties) is consistent with the two mechanistic pathways depicted in Figure 2-1. These differ by which of the two peripheral bonds cleaves initially.

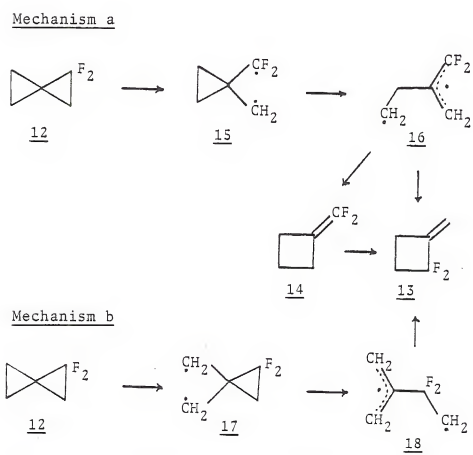


Figure 2-1. Pathways for Rearrangement of 1,1-Difluorospiropentane to 2,2-Difluoromethylenecyclobutane.

In order to determine how much 13, if any, is formed through the competition of mechanism a with mechanism b, an isotopic labeling study was devised.

Thermolysis of the dideuterated compound 19 can reveal, through the distribution of the deuteriums in the product, if there is significant competition by mechanism b (Figure 2-2).

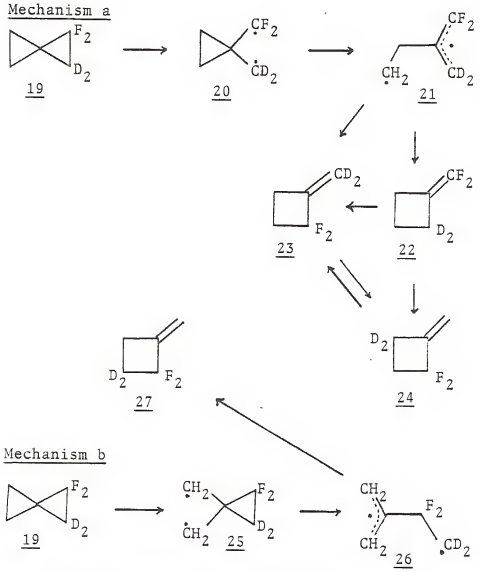
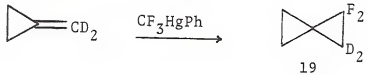


Figure 2-2. Deuterium Distribution According to Mechanism.

Results and Discussion

Synthesis of 19 was achieved through difluorocarbene addition[39] to (dideuteromethylene)cyclopropane.[40]



19

Thermolysis of 19 produced a mixture of the three possible gem-dideuterated 2,2-difluoromethylenecyclobutanes 23, 24 and 27. The identities and relative amounts of these were determined by comparison of the ^{1}H and ^{19}F NMR spectra of the mixture with those of the undeuterated material.

The ^{1}H NMR spectrum of 13 consists of two unresolved multiplets at δ2.43-2.76 which were assigned to the C(3) and C(4) protons, and two vinylic multiplets at δ5.15 and δ5.49. The ratio of vinyl to non-vinyl protons is 1:2. The ^{1}H NMR spectrum of the thermolysis products from 19 shows the same upfield multiplets at δ2.41-2.76 but the vinyl signals are completely resolved into two quintets of doublets at δ5.15 and δ5.47. This pattern is explainable assuming that the allylic F and H coupling constants are each 3Hz. The smaller splitting, J=1.1 Hz, is due to geminal coupling. The ratio of vinyl to non-vinyl protons is 1.0:2.1 which indicates that 23 is present in 37%.

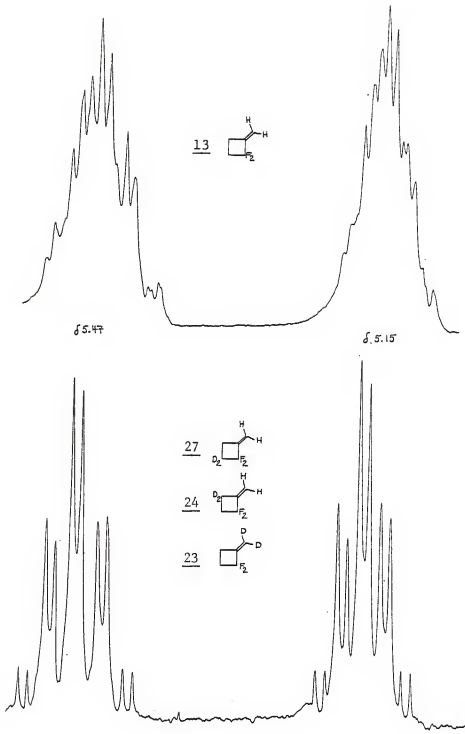


Figure 2-3. Comparison of the Vinylic ^{1}H NMR Signals for 13 and the mixture 23, 24, and 27.

The ratios within these vinylic quintets are 1.0:7.6:16.6:8.1:1.1 which is consistent with superimposition of a triplet from 24 and a quintet from 27, having identical chemical shift and coupling. Figure 2-3 shows a comparison of the vinylic regions of the ^{1}H NMR spectra for the undeterated 13 and the deuterated product mixture of 23, 24 and 27.

The ^{19}F NMR spectrum of the undeuterated 13 shows a complex multiplet at ϕ94.49 with a large vicinal HF coupling to the C(3) protons of 11.8 Hz. The mixture of thermolysis products from 19 shows not only the multiplet described above, but also a second, narrower multiplet at ϕ94.85 which lacks vicinal HF coupling. This new signal is due to the presence of 27 which, in addition to possessing no H vicinal to the fluorines, displays a deuterium isotope effect on the ^{19}F chemical shift. The magnitude and direction of this shift (0.36 ppm upfield) are consistent with those previously observed.[41,42] The ratio of low to high field multiplets is 2.8:1.0, indicating 27 comprises 26% of the mixture. The ^{19}F NMR spectra for the undeuterated 13 and the mixture of deuterated 23, 24 and 27 are compared in Figure 2-4. Knowing the amounts of 23 and 27 present to be 37% and 26% respectively, one then arrives, by subtraction, at 37% for the amount of the remaining isomer 24.

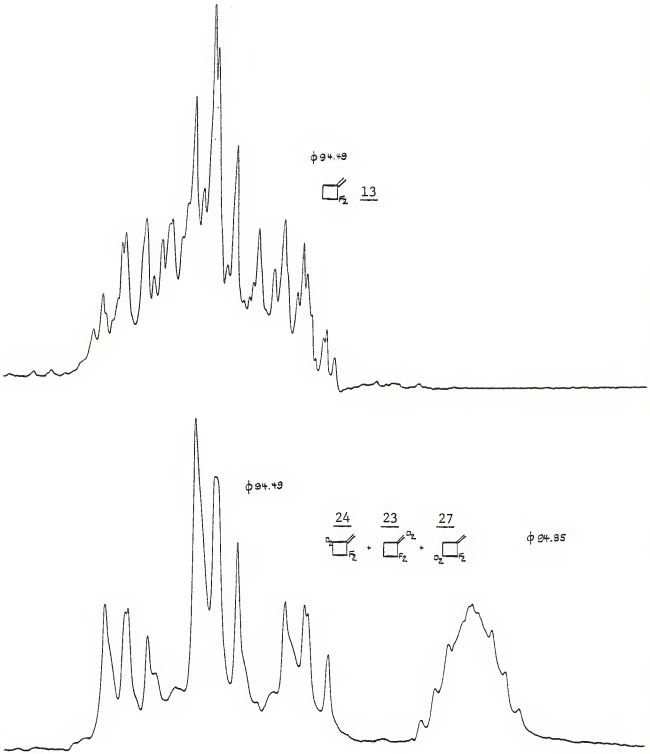
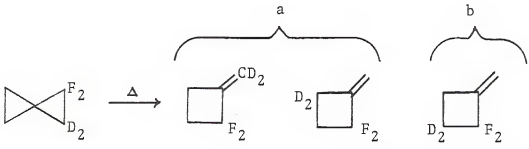


Figure 2-4. Comparison of the ^{19}F NMR Spectrum of 13 to that of the Mixture 23, 24, and 27.

The ratio 37:37:26* for 23:24:27 is consistent with the complete thermal equilibration of 23 and 24 which one would expect under the conditions used for thermolysis of 12.[36] Since products 23 and 24 are formed via mechanism a, and 27 is formed via mechanism b, the product ratio indicates a competition between the two proposed pathways in which a is favored over b by about 3 to 1.



12 23 24 27

37% 37% 26%

*The product ratios, which were established by ^{1}H and ^{19}F NMR integrations have a reliability of ∿±2%.

Samples of 19 and the undeuterated compound 12 were thermolyzed under identical conditions to allow a comparison of their rates (Table 2-2). Rates were determined both by following disappearance of starting material versus an internal standard or alternatively, monitoring product formation. Greater precision was obtained for the latter method and those results were regarded as more reliable.

Table 2-2. Thermal Isomerization of 12 and 19 at 339.6°C.

		$k \times 10^5$, s^{-1} (internal standard)	$k \times 10^5$, s^{-1} (product)
12		3.7147±0.0345	2.7156±0.0196
19		3.3683±0.0316	2.3627±0.0246

The secondary kinetic isotope effect observed (k_H/k_D = 1.15±0.02) is consistent with the majority of the reaction proceeding through initial C(1)-C(2) bond homolysis.*

The results from the thermolyses of 12 and 19 can now take their place among those for other gem-difluorocyclopropanes. The observation of a very slight rate enhancement for cleavage of the C(1)-C(2) bond is consistent with earlier findings.[22]

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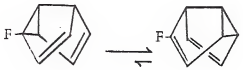
*In a similar but lower E_a rearrangement, the thermal isomerization of dideuterobis(cyclopropylidene) showed a k_H/k_D = 1.21.[40]

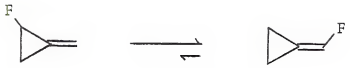
CHAPTER 3
THE KINETIC EFFECT OF FLUORINE ON
THE 1,5 HOMODIENYL HYDROGEN SHIFT

Introduction

In contrast to the wealth of information on gem-difluorocyclopropanes, the studies of the monofluoro derivatives are quite sparce, and these provide information on thermodynamics, rather than kinetics. Paquette's observation of the fluorosemibullvalene equilibrium qualitatively showed that a monofluoro substituent is favored thermodynamically on a double bond rather than a cyclopropane.[43]

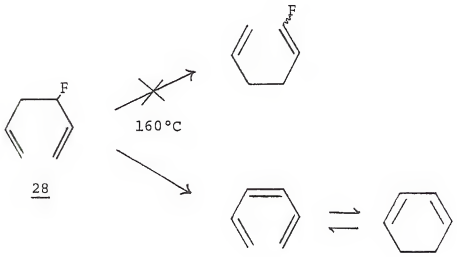


A similar but quantitative study by Dolbier and Burkholder[44] supports this result with the observed equilibrium between the isomeric monofluorinated methylenecyclopropanes.



$\Delta H_r = -2.60 \pm 0.06$ kcal/mol

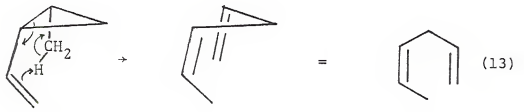
A particular problem in the study of monofluoro systems is that of HF elimination. A monofluoro compound shows a much greater tendency to eliminate HF than does the corresponding gem-difluoro compound. Consider for example the study by Dolbier and Medinger[14] in which the attempted Cope rearrangement of 3-fluoro-1,5-hexadiene could not compete with the rapid formation of HF elimination products.



28

Thermolysis of cis,cis-1-Fluoro-2-methyl-3-vinylcyclopropane

The 1,5 homodienyl hydrogen shift (equation (13)) was selected as a rearrangement in which the kinetic influence of a monofluoro substituent on a cyclopropane might be probed.



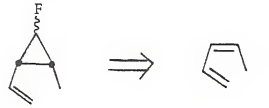
(13)

The mechanistic details of the homodienyl shift have been presented elsewhere.[45-47] Due to the low activation energy for this concerted process the potential problem of HF elimination would be minimized. This system is additionally attractive since kinetic studies on the parent hydrocarbon 29,[45] and the gem-difluorinated compound 30,[29] are available for comparison.

29

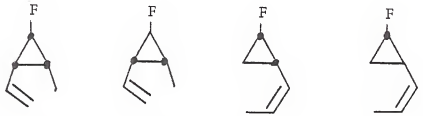
30

A stereochemical requirement for the homodienyl shift is that the carbon bearing the migrating hydrogen be on the same side of the cyclopropane ring plane as the alkene (i.e. cis). Given this restriction, there exist two possible isomeric 1-fluoro-2-methyl-3-vinyl-cyclopropanes which should be accessible from formal addition of fluorocarbene to cis-1,3-pentadiene (14).



(14)

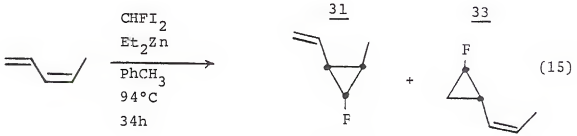
Excluding diadducts, there are four isomeric products one would expect from this synthetic strategy; two regioisomers each of which has two stereoisomers.



31 32 33 34

Results and Discussion

Employing a variation of the method by Nishimura and Furukawa,[48] cis-1,3-pentadiene was heated with $CHFI_2$ in the presence of diethylzinc (15).

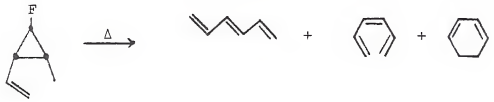


(15)

+ 25% diadducts

In agreement with earlier observations,[48] the predominant mode of addition of the organometallic carbenoid produced cyclopropanes with the fluorine cis to the other groups on the ring. None of the trans monoadducts, 32 and 34 were observed under these conditions.

Gas phase, thermal isomerization of 31 carried out in a well-conditioned pyrex vessel with the results shown in equation (16). Yield was determined by direct GC analysis



(16)

of the gaseous product mixture compared to an internal standard. Products were identified by their ^{1}H, ^{13}C (and their absence of ^{19}F) NMR spectra. Rates of thermal isomerization were measured at six temperatures. Data obtained are given in Table 3-1.

Table 3-1. Rates of Thermal Isomerization for 31.

T,°C	$k \times 10^{4}, s^{-1}$
152.8	1.210±0.030
157.1	1.740±0.043
160.4	2.300±0.063
165.1	2.978±0.082
168.1	3.612±0.183
171.4	5.064±0.046

An Arrhenius plot of the rate data gave a good straight line and the frequency factor and energy of activation were calculated by the method of linear least squares. Activation parameters calculated from rates based on product formation agreed, within experimental error, with those calculated from rates based upon the disappearance of starting material versus an internal standard. Greatest precision was obtained from the latter method, and it is those data which are used throughout this chapter.

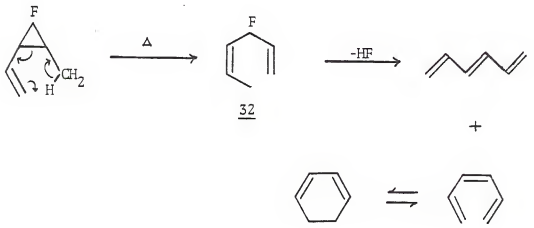
Table 3-2 lists activation parameters and relative rates for the unfluorinated, cis-monofluorinated, and gem-difluorinated species.

Table 3-2. Activation Parameters for 29, 30, and 31.

	E_a kcal/mol	Log A	T_1 °C	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ cal/mol·K	$\Delta G^{\neq}$(166.2°C) kcal/mol	K_{rel} at (166.2°C)
29[a,b]	30.9±0.4 (31.2)	10.9±0.2 (11.0)	166.2-222.1	29.9	-11.7	35.0	(1)
31	27.6±1.2	10.3±0.6	152.8-171.4	26.7	-14.4	33.0	11.2
30[c]	23.3±0.5	10.3±0.3	52.6-86.9	22.7	-13.5	28.6	1540

[a] From a linear least squares treatment of the rate data in ref. 45.
[b] Numbers in parentheses are those reported in ref. 45.
[c] Ref. 29.

These results are most easily explained by the following mechanistic scheme. Initially the 1,5-homodienyl hydrogen shift takes place in a concerted fashion to produce cis-3-fluoro-1,4-pentadiene 32. This bisallylic fluoride then rapidly loses HF to give trans- and cis- 1,3,5-hexatriene, the latter of which equilibrates with 1,3-cyclohexadiene under these conditions.



32

From the data in Table 3-2 one can see that a cis-monofluoro substituent lowers the activation energy for the homodienyl shift by 3.3 kcal/mol and a second fluorine (gem-difluoro) lowers it by an additional 4.3 kcal/mol. At 166.2°C the relative rate of thermolysis is increased only 11-fold by a single fluorine substituent, while an additional 130-fold rate enhancement is observed for 30.

A rationalization for this non-linearity of substituent effect can be found in the following model. Consider the parameters ϕ and θ shown in Figure 3-1.

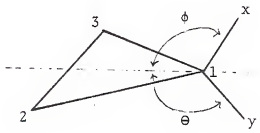


Figure 3-1. Substituent Bond Angles Relative to the Cyclopropane Ring Plane.

These are defined as the angle between the cyclopropane ring plane and the C-x or C-y bond respectively. When x and y are both F, one expects that ϕ and θ will be equal. The bonds to fluorine will be rich in p-character and the resulting rehybridization around C(1) must manifest itself through additional ring strain as the C(2)-C(1)-C(3) valence angle is opened outward.

Now consider the monofluoro case (x = F, y = H). As before the bond to fluorine is richer in p-character and causes a rehybridization around C(1) resulting in an increase in all the angles not involving the C-F bond.* The already strained cyclopropane bonds cannot accommodate the loss of p-character as well as the C(1)-H bond can. One would expect a flattening of the C(1)-H bond relative to the cyclopropane ring, i.e., an increase in θ and a decrease in ϕ. The important point here is that the diminution of p-character in the bonds of C(1) to non-fluorine atoms can be partially compensated by something other than ring strain. By contrast, the gem-difluoro species (x = y = F) does not have this option.

The observed non-additivity of rate enhancement by monofluoro and gem-difluoro substituents also can be explained using a transition state argument. Although the exact nature of the activated complex is not known, it can be reasonably assumed to be some structural hybrid of the reactant and the product. Recall that the IGSTAB values discussed in Chapter 1 are strongly system-dependent. Incremental geminal stabilization by fluorine follows the trend alkyl $\simeq$ allyl >> cyclopropyl > vinyl.[49] As the reaction

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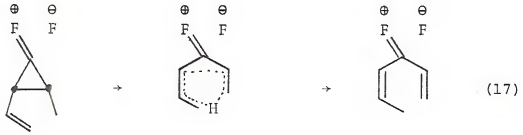
*It may be helpful to consider the (absurd but enlightening) limiting case where the C-F bond is pure p. This would result in sp^2 hybridization around C(1) making C(1), C(2), C(3) and y essentially coplanar with the C-F bond perpendicular to the plane.

proceeds from the cyclopropane to the bisallylic product, it passes through an activated complex which can be represented as 33. This species would be expected to

33 a. x = y = F

b. x = H, y = F

have an IGSTAB for fluorine somewhere between cyclopropyl and allyl. One would predict a lowering of the transition state for 33a relative to that of 33b. Double-bond, no-bond resonance forms (equation (17)), which have no counterparts for the monofluoro species, can be used to rationalize the system-dependence of IGSTAB.

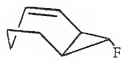


(17)

Thermolysis of endo- and exo-8-Fluorobicyclo[5.1.0]oct-2-ene

In a related study, the thermolyses of 34 and 35 were examined. The hydrocarbon 36, and the gem-difluoro-analogue 37 have been examined previously.

34



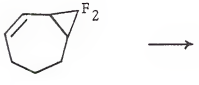
35

36

K_{eq} = 37

E_a = 38.6±0.6 kcal/mol

Log A = 13.3



37

38

$k(152.5°) = 4.47 \times 10^{-4} s^{-1}$

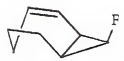
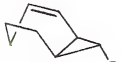
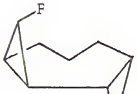
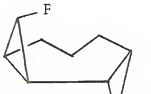
The hydrocarbon undergoes a reversible homodienyl shift for which the activation and equilibrium parameters were determined.[50] The difluoro species 37 was found to rearrange cleanly to 3,3-difluoro-1,4-cyclooctadiene 38 and a rate constant was determined for a single temperature.[29]

Results and Discussion

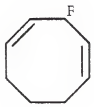
Reaction of 1,3-cycloheptadiene with $CHFI_2$ and diethylzinc yielded the products shown in Table 3-3. The compounds were identified by standard spectral methods.

$$+ \quad CHFI_2 \xrightarrow[\substack{75\text{-}90\,^{\circ}C \\ 43h \\ PhCH_3}]{Et_2Zn}$$

Table 3-3. Reaction Products from 1,3-Cycloheptatriene, $CHFI_2$ and Diethylzinc.

	% Yield
 34	71
 35	9
 39	7
 40	5

Thermolysis of 34 was carried out at three temperatures. The results are given in Table 3-4. Interestingly, neither 41 nor the HF elimination product 42 was observed in the product mixture.

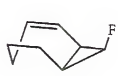


41

42

A single rate was determined for the exo isomer 35 which thermolyzed to give two products with the same GC retention times as 43 and 44 and which appeared in a similar ratio.

Table 3-4. Rate and Product Data for the Thermolysis of 34 and 35.



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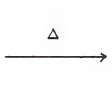
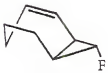


43

44

T,°C	43/44	$k \times 10^4, s^{-1}$
190.0	1.84	1.796±0.059
181.0	1.72	1.199±0.041
175.2	1.54	0.745±0.027
173.8	1.57	0.194±0.045

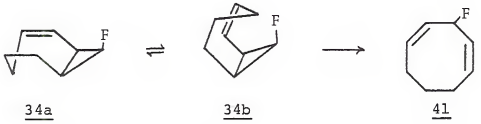


35

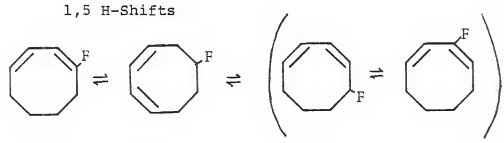
34: E_a = 24.1±3.9 kcal/mol, Log A = 7.63±1.90

k(calculated for 173.8°C) = 7.0×10^{-5} s^{-1}

The observed products are difficult to account for mechanistically (Figure 3-2). Assuming that 34 undergoes the expected homodienyl shift, the primary product formed would be the 1,4-diene 41. There is, however, no obvious mechanism for going from a 1,4-cyclooctadiene to a 1,3-cyclooctadiene. Products 43 and 44 can interconvert with one another (and also the other two isomeric monofluoro 1,3-cyclooctadienes) via 1,5-hydrogen shifts. The problem, then, is reduced to finding a mechanistic entry into 1,3-cyclooctadiene systems from 34.



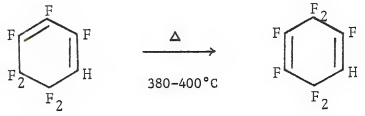
34a 34b 41



43 44 45 46

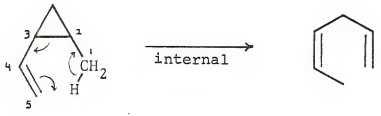
Figure 3-2. Possible Intermediates in the Thermal Rearrangement of 34 to 43 and 44.

A possible conversion of 41 to 45 could involve a 1,3-fluorine shift. Similar 1,3-fluorine shifts, although never unambiguously demonstrated, have been proposed and strongly implicated for the rearrangements of more highly fluorinated compounds. Gas phase thermolysis of 47, for example, has been shown to give 48 as the major product. Control experiments seem to have ruled out the possibility of surface-catalyzed or fluoride ion-promoted reactions.[51]

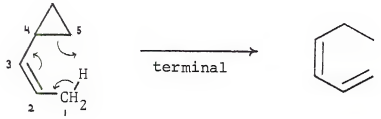


47 48

An alternative mechanism, which does not require the intermediacy of 41, can be visualized by first considering the simplified systems shown in equations (18) and (19). The usual homodienyl hydrogen shift involves, in the simplest case, a methyl vinyl cyclopropane. The cyclopropane bond is in the 2,3 or "internal" position of the 1,5 system (18). Equation (19) shows a different system in which the migrating cyclopropane bond is at the 4,5 or "terminal" position. Neither of these molecules can undergo the reaction depicted for the other. However, a species such as 34 meets the structural requirements for either mechanism.



(18)



(19)

Figure 3-3 shows an additional factor which may help account for the unusual products. In order to yield the observed product with cis double bonds in the ring, the usual internal homodienyl shift is required to proceed via the "saddle" conformation 34b[47] in which the cross-ring Van der Waals interactions are unfavorable. Molecular models show that a lower energy conformer 34a has good geometrical disposition for the terminal homodienyl shift and can give a cis,cis-1,3-cyclooctadiene. A product formally derivable from such a terminal homodienyl shift

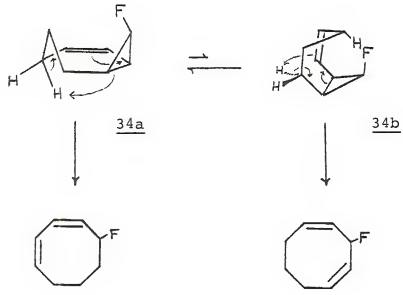


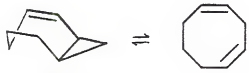
Figure 3-3. Conformations for Internal and Terminal Homodienyl Shifts.

has been observed previously. Dolbier and Sellers[28] reported 4,4-difluoro-1,3-hexadiene 49 as a thermolysis product of 50.

50 49

It is not obvious why the internal homodienyl pathway should be favored for both the hydrocarbon[50] and the gem-difluoro compound[29] while the terminal pathway is implicated for 34 and 35. Table 3-5 compares the activation parameters and rates for these systems. Such a comparison must, however, be approached cautiously due to the large uncertainties in the activation parameters determined for 34 and the suggestion of an alternative mechanism for that species.

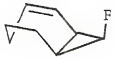
Table 3-5. Activation Parameters and Relative Rates for Thermal Isomerization of 34, 36 and 37.



36

E_a = 38.6±0.6 kcal/mol

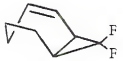
Log A = 13.3



34

E_a = 24.1±3.9 kcal/mol

Log A = 7.6±1.9



37

$k_{152.5°} = 4.47 \times 10^{-4}\ s^{-1}$

ID #	k(152.5°), s^{-1}	k_{rel}
36	3.25×10^{-7}	1
34	1.68×10^{-5}	52
37	4.47×10^{-4}	1400

CHAPTER 4
DIFLUORODIIODOMETHANE: PREPARATION, PROPERTIES, AND POTENTIAL USES

Introduction

Fluorodiiodomethane, $CHFI_2$, has been shown to be a useful reagent for the preparation of monofluorocyclopropanes.[48] Hine et al. reported obtaining $CHFI_2$ in 32% yield from the reaction of neat iodoform heated to 120°C and treated with solid mercuric fluoride followed by distillation of the product at reduced pressure.[52]

$$2CHI_3 + HgF_2 \rightarrow 2CHFI_2 + HgI_2$$

It was thought that a variation of this method might produce better results. An apparatus which would allow the reaction to be run at 120°C and under reduced pressure provided the possibility for continuous removal of the product as it was formed, thus minimizing the formation of CHF_2I and CHF_3.

As expected, this procedure gave $CHFI_2$ in an improved yield of 47%. Also found were the unexpected products diiodomethane and difluorodiiodomethane.

$$CHI_3 \xrightarrow[120°]{HgF_2} \underset{47\%}{CHFI_2} + \underset{6\%}{CH_2I_2} + \underset{6\%}{CF_2I_2}$$

That the two minor products were formed in an essentially aprotic medium and appear in equal amounts suggests that they are secondary products resulting from the disproportionation of $CHFI_2$.

$$2CHFI_2 \rightarrow CH_2I_2 + CF_2I_2$$

Interest in CF_2I_2 arose from its possible synthetic utility (Figure 4-1). Besides having potential as a difluorocarbene precursor, CF_2I_2 was expected to undergo free radical additions to olefins to produce adducts 51 which in turn might be reduced to primary gem-difluorides 52 or reductively coupled to yield gem-difluorocyclopropanes 53.

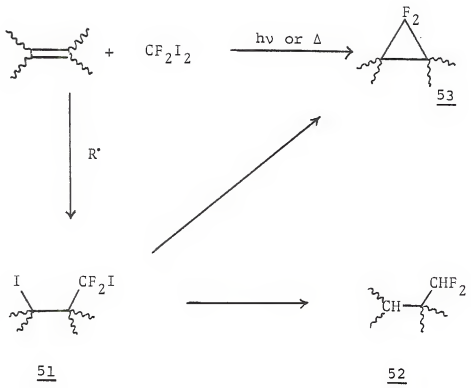


Figure 4-1. CF_2I_2 as a Synthetic Reagent.

A literature search on CF_2I_2 revealed another surprising fact. Contrary to what its simple formula would suggest, CF_2I_2 has previously been available in only small amounts via difficult and low-yield procedures involving the γ-irradiation of CF_3I [53,54] or the addition of difluorocarbene to molecular iodine.[55-58] Clearly any routine use of CF_2I_2 requires a more practical source.

Results and Discussion

Preparation

As expected from analogy to the preparation of $CHFI_2$ from CHI_3,[52] treatment of the readily available CI_4[59,60] with HgF_2 produced CF_2I_2 in fair yield.

$$CI_4 + HgF_2 \xrightarrow[27\%]{25\text{-}110\,^{\circ}C} CF_2I_2 + HgI_2$$

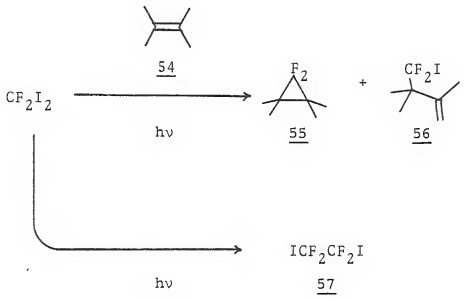
An attempt to carry out this transformation using a 9:1 molar ration of KF/HgF_2 gave unsatisfactory results.

Properties

Difluorodiiodomethane is a pale yellow liquid which at room temperature or upon exposure to light quickly acquires the characteristic burgundy color of I_2-containing solutions. It boils at 39-41°C (80 torr) and has a vapor pressure of 28 torr at 25°C. Although refrigeration is recommended, only minor decomposition (<2%) is observed when CF_2I_2 is stored at room temperature in a pyrex flask for several weeks. It is stable indefinitely at -78°C and is miscible with most organic solvents. Detailed spectral data are given in the experimental chapter.

Photolyses

Photolysis of CF_2I_2 in the presence of 2,3-dimethyl-2-butene 54 under various conditions (see experimental) gave 55 and 56. In the absence of olefins, photolysis of CF_2I_2 yields 57 and I_2.



These observations are most easily rationalized through the processes shown in Figure 4-2.

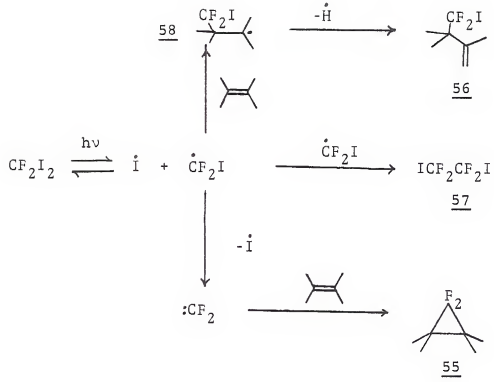
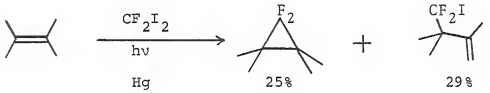


Figure 4-2. Mechanisms of CF_2I_2 Photolysis.

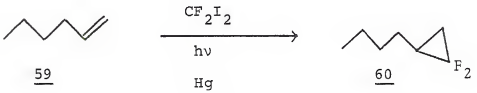
Initial photodissociation of CF_2I_2 produces a difluoroiodomethyl radical and an iodine atom. The $\dot{C}F_2I$ then has several possible fates. It can be captured by the olefin to give a radical intermediate 58 which then loses a hydrogen atom to give 56. It can lose a second iodine atom to produce difluorocarbene which is then trapped by the olefin to give 55. It can couple to another $\dot{C}F_2I$ to give 57. Finally, it can couple to an iodine atom to regenerate the starting material.

The highest yields of 55 obtained photochemically were through the use of Hg or $NaOH_{(aq)}$ as iodine scavengers.



Analogous reactions have been reported for CH_2I_2 [61] and $CHFI_2$.[62]

Less satisfactory results were obtained when 1-hexene was reacted under these conditions. Only a trace amount of the desired cyclopropane 60 was detected.



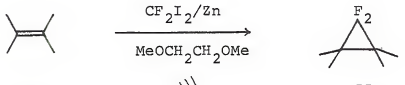
59 60

Thermolysis

Difluorodiiodomethane is not a good thermal source of difluorocarbene. When a sample of CF_2I_2 was heated at 87°C for 32h with excess 54, no significant reaction was observed and the CF_2I_2 was recovered in >85%.

Simmons-Smith reactions

When CF_2I_2 was used in place of CH_2I_2 for a modified Simmons-Smith reaction,[63] 54 was converted to 55 in a very modest yield (3% by NMR). A recent report that Simmons-Smith cyclopropanations with CH_2I_2 are facilitated by ultrasonic irradiation[64] suggested that a similar enhancement might be observed for CF_2I_2. When the reaction of 54 with CF_2I_2 and Zn was carried out in a sonicator, the yield was improved more than 12-fold.



54 55

Free-radical additions

As expected, CF_2I_2 proved to be an excellent reagent for free-radical chain additions to alkenes. Its addition to 1-hexene and methyl propenoate proceeded smoothly in 73% and 47% isolated yields respectively. These reactions have analogy in the addition of CF_2Br_2 to alkenes[65] but are cleaner in that telomerization is not a significant side reaction.

$$CH_2{=}CH(CH_2)_3CH_3 + CF_2I_2 \xrightarrow[(BzO)_2]{\Delta} CF_2ICH_2CHI(CH_2)_3CH_3$$

73%

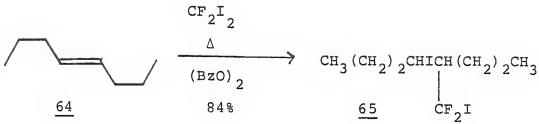
59 61

$$CH_2{=}CHCO_2CH_3 + CF_2I_2 \xrightarrow[(BzO)_2]{\Delta} CF_2ICH_2CHICO_2CH_3$$

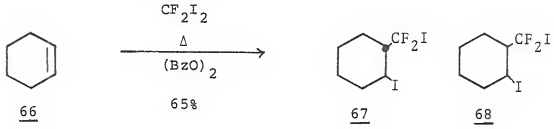
74%

62 63

Similar reactions of CF_2I_2 with internal olefins such as trans-4-octene and cyclohexene were also quite successful. However, its attempted addition to 54 resulted in the exclusive formation of 56, likely via diversion of the expected radical intermediate 58 by H atom abstraction.

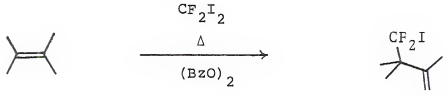


64 65



66 67 68

(67/68 = 70:30)

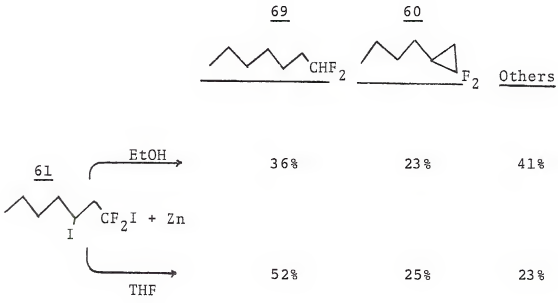


54 95% 56

Reduction of radical adducts

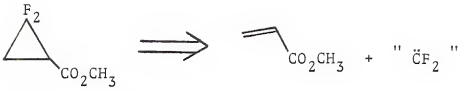
With the radical adducts 51 so readily accessible, it seemed worthwhile to devise methods for their conversion to primary gem-difluorides 52 or gem-difluorocyclopropanes 53. Analogous reductions of alkyl iodides to alkanes[66] and intramolecular reductive couplings of α,γ-diiodides to cyclopropanes[67-69] are known.

Treatment of 1,1-difluoro-1,3-diiodoheptane 61 with Zn in refluxing ethanol gave 1,1-difluoroheptane 69 and 1-butyl-2,2-difluorocyclopropane 60 along with a variety of mostly unidentified side products. A cleaner reaction occurs when it is carried out in THF and the relative amount of 69 produced is enhanced.



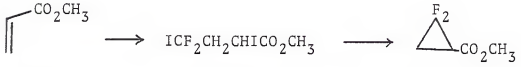
(Relative yields)

Reductive couplings of the type 61 → 60 are especially interesting and useful in that they provide a route into gem-difluorocyclopropanes that does not require difluorocarbene addition. Consider, for example, ester 70.



70 62

One would retrosynthetically view this as having come from CF_2 addition to methyl propenoate 62. Unfortunately, all of the usual methods for formal CF_2 addition to alkenes are notoriously unsuccessful with electron deficient olefins.[1,70] An alternative route to 70 would involve radical addition of CF_2I_2 to 62 followed by reductive coupling of the resulting diiodide 63.



62 63 70

Summary

Difluorodiiodomethane is now available in quantities that make it a practical laboratory reagent. It can be produced in fair yield by the treatment of CI_4 with HgF_2.

As a difluorocarbene synthon, CF_2I_2 has been used for photochemical and Simmons-Smith cyclopropanations. Although the generality of these reactions has not been verified, fair yields of gem -difluorocyclopropane 55 have been achieved with alkene 54.

Difluorodiiodomethane undergoes facile free-radical additions to alkenes. Isolated yields of 47 - 84% are obtainable from the addition of CF_2I_2 to various mono-substituted and disubstituted olefins.

54

55

CHAPTER 5
EXPERIMENTAL

General

NMR spectra were recorded on a Nicolet NT-300, a Jeol FX-100, a Varian XL-100 or a Varian EM 360L spectrometer. ^{1}H and ^{13}C chemical shifts (δ) are reported as ppm downfield of internal TMS. ^{19}F chemical shifts (ϕ) are reported in ppm upfield of internal $CFCl_3$. All NMR spectra were obtained at ambient temperature in $CDCl_3$ unless otherwise specified. Where ^{19}F NMR yields are reported, a predetermined amount of m-bromobenzotrifluoride (Columbia Chemical Co.) was used as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer from films of neat liquids between KBr plates. Mass spectra and exact masses were determined on an AEI-MS 50 spectrometer at 70 eV and are reported as m/q(% rel. base)fragment. Unless otherwise specified all photolyses were carried out in a Rayonet® photochemical reactor with 350 nm source lamps.

Preparation of 1,1-Dideutero-2,2-difluorospiropentane, 19

Into a small carius tube were placed 1.16g of CF_3HgPh [39] (3.34 mmol), 1.58g of NaI (10.5 mmol), 0.18g of (dideuteromethylene)cyclopropane[40] (3.21 mmol), about 1.5 ml of benzene (freshly distilled from CaH_2 onto molecular

sieves), and a few mg of $Bu_4N^{\oplus}I^{\ominus}$. The tube was sealed under vacuum and suspended in a preheated oil bath equipped with a mechanical stirrer. The tube was situated such that the blades of the stirring propeller could vibrate against it and provide agitation for the reacting mixture. After 48h of heating at 85-88°C, the tube was opened and all volatile material was vacuum transferred to a small flask. The product 19 was isolated by preparative GC (10% tricresylphosphate, 80°C, 15' x 0.25", He flow = 60 mL/min) in 40% yield.

^{1}H NMR: δ 1.15 (m)

^{19}F NMR: ϕ 135.69 (m)

^{13}C NMR: δ 114.56 (t,J = 285.2 Hz, CF_2)

δ 15.3 (m, CD_2)

δ 27.6 (v weak, tentatively identified as spiro C)*

δ 6.47 (s, C_3 and C_4)

IR: 700, 740, 960, 1060, 1210, 1255, 1450, 1550, 3025, 3100 cm^{-1}.

MS: High resolution mean of 11 scans

M^+ = 106.05571, std dv ± 0.00248 (23.4 ppm)

Calculated $C_5H_4F_2D_2$ = 106.05631

dev = -0.00060(-5.7 ppm)

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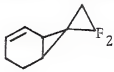
*Model compound 71 shows a spiro ^{13}C resonance at δ 25.1. Henryk Koroniak, unpublished results, 1982, Univ. of Fl.

71 = 

Thermolysis of 1,1-Dideutero-2,2-difluorospiropropane 19

The thermolysis of 19 was carried out in a well-conditioned, spherical, pyrex vessel of approximately 200 mL capacity, submerged in a stirred, thermostated, molten salt bath (eutectic mixture 50/50 by weight of $NaNO_2$ and KNO_3, mp ≈ 150°). The temperature was measured using a chromel-alumel thermocouple in conjunction with a Tinsley type 3387E potentiometer. The thermocouple was immersed in a well next to the thermolysis vessel. The temperature was controlled to ±0.1°C using a Hallikainen (now TOTCO) Instrument Thermotrol proportional controller with a model 1256A platinum resistance probe. Product identification was done by standard spectroscopic methods on material from preparative runs in which 40 torr of 19 were expanded into the pyrolysis vessel through a contiguous vaccum line and thermolyzed for 5 to 6 half-lives. A mixture of 23, 24 and 27 was purified by preparative GC (10% ODPN, 20' x 0.25", 35°, He flow = 30 mL/min). Compounds 23, 24, and 27 were identified by their NMR spectra which were similar to those of the undeuterated 13 (See discussion in text). For kinetics, a mixture of approximately 10 torr of 19 and the internal standard pentane, was stirred for several hours in an isolated section of the vacuum line and checked by GC for homogeneity before expanding the mixture into the thermolysis vessel.

The kinetic run was sampled at convenient intervals by removing small fractions of the pyrolysis mixture by expansion through a small section of the vacuum line into a gas storage bulb and diluting with argon. This sample bulb was removed and used to make multiple GC injections through a gas sampling valve. A Hewlett-Packard 5710A gas chromatograph with a flame ionization detector was used in conjunction with an HP-3380S integrator for the anlaysis. Baseline resolution of peaks was observed. Each point in the rate constant is an average of at least 3 GC runs. The rate constant plot contained 6 points and was derived by a linear least squares analysis of the experimental data yielding a correlation coefficient of 0.9998.

Comparative Rate for Thermolysis of 1,1-Difluorospiropentane 12

For comparison purposes, a thermolysis of the undeuterated material 12 was carried out in the manner described above at the same temperature on the same day. Samples of the reaction mixture taken at six times gave a plot with a correlation coefficient of 0.99989.

Preparation of cis,cis-1-Fluoro-2-methyl-3-vinylcyclopropane 31

The following procedure was patterned after that of Nishimura and Furukawa.[48] A 50-mL 3-necked flask was equipped with a nitrogen inlet stopcock, a dry ice condenser, a magnetic stirring bar, and a rubber septum. The outlet

of the condenser was connected to a mineral oil, U-tube bubbler. The glassware used for the apparatus was dried in an 120°C oven and assembled hot, then cooled to ambient temperature under a slow flow of dry nitrogen. The nitrogen flow was discontinued and, with standard syringe technique,[71] the following reagents were placed in the reaction flask: 20 mL 1.6 M diethylzinc in toluene (32 mmol, Aldrich, Caution! extremely pyrophoric), 4.0 mL cis-1,3-pentadiene (40 mmole, Fluka), and 2.7 mL $CHFI_2$[52] (8.5g, 30 mmol). The condenser was filled with dry ice and the reaction mixture was magnetically stirred. Reaction progress was monitored by anaerobically syringing out a small sample of the mixture into a septum-capped NMR tube and examining it by ^{19}F NMR for disappearance of $CHFI_2$ (ϕ102, d, J=48 Hz). The sample could then be placed back into the reaction mixture. No reaction was observed to occur at room temperature after 16h. The reaction mixture was heated to 94°C for 15h, and an additional 1 mL of neat diethylzinc[72] was added by syringe followed by another 19h of heating. The reaction flask was cooled to 0°C and the mixture was slowly quenched (caution!) with approximately 30 mL of 0.75 M HCl and transferred to a separatory funnel. The organic layer was washed thrice with 0.75 M HCl and thrice with distilled water then dried over $CaCl_2$. The resulting solution was examined by ^{19}F NMR and yields were determined by integration. Samples of the products were isolated by preparative GC (20% Diisodecylphthalate, 10' x 0.25", 73°, 30 mL/min He flow).

31, 35%

^{1}H NMR δ 4.63 (dt, J=65.5 Hz, J=5.8 Hz, 1H, FC-H)

δ 1.12 (m, 3H, CH_3)

δ 1.48 - 1.60 (m, 1H, allylic)

δ 1.02 - 1.16 (m, 1H, MeC-H)

δ 5.66(dddd, J=17.2 Hz, J=10.4 Hz, J=9.3 Hz, J=1 Hz, 1H, internal vinyl)

δ 5.24 (dd, J=17.2 Hz, J=2.1 Hz, 1H, terminal vinyl cis to cyclopropyl)

δ 5.15 (dd, J=10.4 Hz, J=2.1 Hz, 1H, terminal vinyl trans to cyclopropyl).

^{19}F NMR:φ237.1 (dt, J=65.6 Hz, J=7 Hz)

^{13}C NMR:δ130.6 (d, J=8.5 Hz, internal olefinic)

δ117.0 (s, terminal olefinic)

δ 74.6 (d, J=221 Hz, CHF)

δ 22.7 (d, J=9.8 Hz, allylic)

δ 15.6 (d, J=11.0 Hz, C-Me)

δ 5.8 (d, J=8.6 Hz, CH_3)

IR: 285(wk), 330(wk), 710(wk), 730, 780, 860, 905, 970, 990, 1015, 1045, 1075, 1115(wk), 1145, 1180, 1230, 1330, 1390, 1460, 1635, 1695, 2880, 2940, 2960, 2990, 3010, 3040, 3085 cm^{-1}.

MS: 100 (30.2) M^+

85 (100) M^+-CH_3

79 (10.6)

72 (17.3)

65 (18.8) C_5H_5

59 (37.7) C_2H_2F

53 (17.4)

51 (11.4)

46 (9.3)

41 (20.7)

39 (46.2) C_3H_3

27 (20.7) C_2H_3

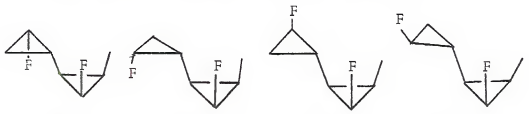
33, 21%

^1H NMR δ 4.65 (dtd, J=66 Hz, J=7 Hz, J= 4 Hz, FC-H)

δ 4.8 - 5.9 (m, vinylic)

^{19}F NMR ϕ223.5 (ddddd, J=65.0 Hz, J=23 Hz, J=12.3 Hz, J=5.0 Hz, J=1.1 Hz)

At least four isomeric diadducts which were not separable by GC were also observed (24%). The chemical shifts and coupling patterns from the ^{19}F NMR spectrum of a mixture of these were consistent with the presence of approximately 11-12% each of the syn, syn diadducts 72 and 73 and approximately 1% each of the syn, anti diadducts 74 and 75 (Table 5-1).



72 73 74 75

Table 5-1. ^{19}F NMR Data from Mixture of Diadducts.

ϕ	Description	% rel intensity
207.0	dtd, J=64.0 Hz, J=21,4 Hz, J=10.5 Hz	1
208.0	dtd, J=64.2 Hz, J=21.7 Hz, J=10.0 Hz	2
224.7	m, at least 2 different F's, unresolved, syn environment for each i.e., dt J≈65 Hz, J≈10 Hz	47
239.0	m, several different F's, unresolved, syn environment for each i.e., dt J≈65 Hz, J≈10 Hz	50

Thermolysis of cis,cis-1-Fluoro-2-methyl-3-vinylcyclopropane 31

The gas phase thermolyses of 31 were carried out as was described for that of 19 above except the internal standard used was methylcyclohexane and GC analyses were performed using a Hewlett-Packard 5790A series gas chromatograph with gas injection system and flame ionization detector in conjunction with a Hewlett-Packard 3390A integrator. The column was 10' x 0.125", 10% β,β-oxydipropionitrile on chromosorp WHP at 60°C, with 5.5 mL/min N_2 flow. A preparative run showed, assuming uniform detector response, 99% material

balance by internal standard after 7.2 half-lives. A sample of the gaseous reaction mixture was taken directly from the thermolysis vessel without condensing and examined by GC/MS. Only C_6H_8 products, starting material, and internal standard coud be detected. One preparative run was condensed directly into an NMR tube, which was then sealed at -196°C. The sample was maintained at -50°C or below until NMR analysis was complete. Only elimination products were observed. These were identified by their ^1H and ^{13}C NMR spectra.

Preparation of endo- and exo-8-Fluorobicyclo-[5.1.0]oct-2-ene, 34 and 35.

A procedure similar to that described above for the preparation of 31 was used. Into an oxygen-free apparatus were syringed 2.8 ml of 1,3-cycloheptadiene (26 mmol, Aldrich), 12.5 ml of 1.6 M diethylzinc in toluene (20 mmol, Aldrich) and 5.0g of $CHFI_2$[52] (17.5 mmol). The magnetically stirred mixture was heated at a pot temperature of 75-90°C for 43h. In addition to 8% unreacted $CHFI_2$, the following products were obtained by preparative GC (20% carbowax, 20' x 0.25", 135°C, 60 mL/min He flow).

34, 71%

^1H NMR: δ 4.50 (dt, J=66 Hz, J=6 Hz, 1H, FC-H)

δ 4.30 - 4.75 (m, 2H, vinylic)

δ 0.85 - 2.42 (m, 8H)

^{19}F NMR: ϕ 234 (dt, J=66.9 Hz, J=6.7 Hz)

^{13}C NMR: δ 132.4 (s, C_3)

δ 122.2 (d, J=5.1 Hz, C_2)

δ 73.7 (d, J=220.9 Hz, C_8)

δ 29.0 (s, C_4)

δ 23.7 (s, C_5)

δ 19.6 (d, J=7.0 Hz, C_6)

δ 18.3 (d, J=9.6 Hz, C_1)

δ 18.2 (d, J=10.9 Hz, C_7)

IR: 585, 690, 710, 880, 1005, 1040, 1115, 1125, 1195, 1225, 1410, 1450, 1665, 2870, 2940, 3005 cm^{-1}

MS: M^+ 126.0845 std dev = $\pm$ 0.00065 ($\pm$ 5.2 ppm)

mean of 10 scans

Calculated for $C_8H_{11}F$ = 126.08448

dev = 0.00003 (+ 0.2 ppm)

126 (15.9) M^+

111 (21.0)

98 (17.5)

97 (37.2)

93 (57.1)

91 (24.0)

85 (19.0)

79 (26.1)

67 (11.8)

65 (11.7)

59 (13.4)

39 (23.0)

35, 9%

^{1}H NMR: δ 4.22 (dt, J=64.6 Hz, H=2.2 Hz, 1H, FC-H)

δ 5.32 - 5.58 (m, 1H, C_2-H)

δ 5.62 - 5.84 (d br s, 1H, C_3-H)

δ 1.0 - 2.15 (br unresolved m)

^{19}F NMR:φ199.6 (dt, J=64.8 Hz, J=44 Hz)

^{13}C NMR:δ130.6 (d, J=3.1 Hz)

δ125.4 (d, J=0.7 Hz)

δ 79.7 (d, J=231.1 Hz, C_8)

δ 30.4 (s, C_4)

δ 26.5 (s, C_5)

δ 26.1 (d, J=9.0 Hz, C_1)

δ 25.0 (d, J=1.7 Hz, C_6)

δ 24.2 (d, J=11.2 Hz, C_7)

IR: 690, 710, 1105, 1380, 1450, 1640, 2860, 2920, 2960, 3010 cm^{-1}

MS: M^+= 126.08473 std. dev. = ± 0.00065 (± 1.5 ppm)

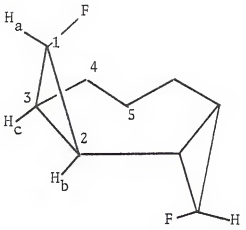
mean of 9 scans

Calculated $C_8H_{11}F$ = 126.08448

dev. = -0.00025 (-2.0 ppm)

126(5.7)M^+, 67 (100,base) C_5H_7, and many others

39, 7%



^{1}H NMR: δ 4.59 (dt, J=66.2 Hz, J=6.2 Hz, 2H, H_a)

δ 1.58 - 1.80 (br s, 6H, H's on C_4 and C_5)

δ 0.91 - 1.03 (m, 2H, H_b)

δ 0.68 - 0.81 (m, 2H, H_c)

^{19}F NMR: φ237.4 (dt, J=66.2 Hz, J=5.9 Hz)

^{13}C NMR: δ 73.0 (d, J=223.4 Hz, C_1)

δ 23.2 (s, C_5)

δ 17.9 (d, J=8.5 Hz, C_4)

δ 15.0 (d, J=11.0 Hz, C_3)

δ 10.6 (dd, J=10.4 Hz, J=7.9 Hz, C_2)

IR: 530, 565, 605, 615, 740, 775, 785, 835, 930, 990, 1025, 1070, 1140, 1190, 1220, 1360, 1405, 1455, 2870, 2930, 2960, 3010, 3050 cm^{-1}

MS: M^+= 158.0910 std. dev. = ± 0.0018 (14.5 ppm)

mean of 13 scans

Calculated for $C_9H_{12}F_2$ = 158.09070

dev. = +0.00029 (+ 1.9 ppm)

86 (100) base peak

40, 5%

This material was not isolated by preparative GC, but was observed in the reaction mixture by NMR

^{19}F NMR δ237.3 (dt, J=65.7 Hz, J=6 Hz, endo F)

δ203.5 (dt, J=64 Hz, J=21 Hz, exo F)

Thermolyses of endo- and exo-8-Fluorobicyclo-[5.1.0]oct-2-ene

The procedure and apparatus were the same as those described for the thermolysis of 19 except that because of the low vapor pressures of 34 and 35, the sample bulbs had to be heated to about 50°C in order to maintain good reproducibility of GC injections. The sampling bulbs were wrapped with Thermolyne, BriskHeat® silicon rubber embedded flexible electrical heating tape and covered with a blanket of plaster of Paris. All portions of the sampling area, kinetics line, and gas injection system were maintained at about 50°C. A maximum vapor pressure of 4 to 5 torr could be obtained and was used for all kinetic and preparative runs. One preparative run was carried out on 34 with 5 torr of nonane present as an internal standard and, assuming uniform defect response, >95% material balance was observed after 7.5 half-lives. Several preparative runs were performed consecutively and condensed into a small flask. The resulting products were isolated by preparative GC (20% dinonylphthalate, 135°, 20' x 0.25", 60 mL/min He flow).

43

^{1}H NMR: δ 5.78 (m, 1H, C_2-H)

δ 5.61 (dt, J=10.8 Hz, J=7.7 Hz, 1H, C_4-H)

δ 5.46 (dd, J=21.0 Hz, J=4.7 Hz, 1H, C_3-H)

δ 2.34 (m, 2H, C_8-H)

δ 2.24 (m, 2H, C_5-H)

δ 1.67 (m, 2H)

δ 1.51 (m, 2H)

^{13}C NMR: δ 161.3 (d, J=252.5 Hz, C_1)

δ 130.8 (d, J=2.0 Hz, C_4)

δ 122.9 (d, J=12.4 Hz, C_3)

δ 102.9 (d, J=27.1 Hz, C_2)

δ 30.0 (d, J=28.5, C_8)

δ 26.8 (s, C_5)

δ 24.8 (s, C_6)

δ 20.7 (d, J=4.9 Hz, C_7)

^{19}F NMR: ϕ 90.9 (m)

44

^{1}H NMR: δ 6.00 (dd, J=11.1 Hz, J=4.1 Hz, 1H)

δ 5.77 (dd, J=12.0 Hz, J=4.] Hz, 1H)

δ 5.72 - 5.55 (m, 2H)

δ 2.78 - 1.42 (m, 6H)

^{13}C NMR: δ 131.5 (s, C_3)

δ 129.9 (s, C_2)

δ 125.6 (d, J=10.3 Hz, C_4)

δ 125.1 (s, C_1)

δ 90.4 (d, J=169.5 Hz, C_6)

δ 33.2 (d, J=22.8 Hz, C_5)

δ 28.2 (d, J=21.2 Hz, C_7)

δ 23.7 (d, J=8.0 Hz, C_8)

^{19}F NMR: ϕ 172 (m)

Reaction of CHI_3 with HgF_2

Into two solid addition tubes were placed a total of 99.1 g of HgF_2 (0.415 mol, Alfa Products). These were inserted into a 500-mL 3-necked flask containing a large stirring magnet and 349.3 g of solid CHI_3 (0.8872 mol), and equipped with a distillation head. The system was evacuated to 50 torr, and the reaction flask was heated over an oil bath at approximately 140°C until nearly all the CHI_3 had melted. The temperature was decreased to 120°C and the solid HgF_2 was added gradually to the magnetically stirring CHI_3 melt over a 40 minute period. A dark burgundy-colored distillate was collected at 60° to 80° in a 200-mL receiving flask which was cooled to 0°. Approximately 60 mL of distillate (154g) were collected. This material was washed twice with aqueous $Na_2S_2O_3$ and then fractionally vacuum distilled to produce 111g of $CHFI_2$ (47%, BP=55-65°, 50 torr) and 6% each of CF_2I_2 (BP=29-33,50 torr), and CH_2I_2 (BP=>75°, 50 torr).

Preparation of CF_2I_2

Into a 500-mL three-necked flask equipped with distillation head and vacuum Hershberg stirrer were placed 142.4g of $Cl_4{}^{59}$ (0.274 mol) and 69.6g of HgF_2 (0.292 mol). The flask was closed off with a 125-mL pressure-equalizing addition funnel containing 100 mL of 1,2-dichlorobenzene.* The system was evacuated to 50 torr through a -78°C trap, and the dichlorobenzene was added slowly (exothermic as reactions begin!) until the heterogeneous system was wet enough to stir easily (ca. 80 mL). (In an alternative procedure a solid addition tube was used to slowly add HgF_2 to a stirring solution of CI_4). Heating at 100°C produced a dark purple distillate which came over at 50-81°C (50 torr) into a receiving flask cooled to 0°C. Distillation ceased after about 45 min.** The trap contents and distillate were combined with those from a previous run (0.270 mol of CI_4 and 0.273 mol of HgF_2) and distilled under vacuum: yield 44.8g (27%); bp 39-41°C (80 torr). Small amounts of crude CF_2I_2 can be purified (i.e., freed from I_2) as needed by

*Other inert, high-boiling solvents (e.g. perfluorodecaline or $n\text{-}C_8F_{17}SO_2F$) can also be used.

**Higher isolated yields can be obtained by claiming the small amount of CF_2I_2 remaining in the reaction mixture. This can be done by slowly pulling a vacuum above the stirring mixture at room temperature through a -78° trap followed by vacuum distillation of the trap contents.

trap to trap distillation under high vacuum through a 0, -40, -78, and -196°C trap system. Pure CF_2I_2 is found in the -78°C trap. It has a vapor pressure of 28 torr at 25°C.

^{19}F NMR:ϕ -18.6 (s)

^{13}C NMR:δ 2.29 (t, J=378 Hz)

MS: 304 (28) M^+

285 (3.6) CF_2I

254 (24) I_2

177 (100) CF_2I

158 (3.0) CFI

127 (36) I

50 (2.2) CF_2

IR: 720, 1045, 1095 cm^{-1}

Photolyses of CF_2I_2

Photolysis of CF_2I_2 with 2,3-Dimethyl-2-butene 54 and Hg

Into a small Carius tube were weighed 0.30g of CF_2I_2 (0.99 mmol), 1.33g of 2,3-dimethyl-2-butene (16 mmol), and 0.87g of Hg (4.4 mmol). The reaction mixture was thoroughly degassed, and the tube was sealed under vacuum. The mixture was photolyzed for 23h with occasional shaking. Afterward the tube was opened, and all volatile material was vacuum transferred and analyzed by ^{19}F NMR. The product mixture contained 25% 1,1-difluoro-2,2,3,3-tetramethylcyclopropane 55 and 29% 4,4-difluoro-4-iodo-2,3,3-trimethyl-1-butene 56. Pure samples of each were isolated by preparative gas chromatography (20% dinonyl phthalate on Chromosorb WHP, 20' x 0.25", 110°C).

55

The ^{1}H NMR (δ 1.1, t, J=2 Hz) and the ^{19}F NMR (ϕ149) spectra were identical with those reported for 55.[73,74]

56

^{1}H NMR: δ 5.09 (br s, 1H, vinylic)

δ 5.05 (br s, 1H, vinylic)

δ 1.85 (dd, J=3.3 Hz, J=1.5 Hz, 3H, allylic)

δ 1.29 (t, J=0.8 Hz, 6H, methyls on C_3)

^{19}F NMR: ϕ 41.5 (br s)

^{13}C NMR: δ 145.5 (br s, C_2)

δ 116.3 (s, C_1)

δ 114.5 (t, J=322 Hz, C_4)

δ 52.7 (t, J=15.9 Hz C_3)

δ 23.1 (t, J=3.7 Hz, methyls on C_3)

δ 21.3 (t, J=3.1 Hz, allylic methyl on C_2)

IR: 575, 770, 860, 925, 1070(s), 1215, 1385, 1450, 1640(w), 2960 cm^{-1}

MS: $M^+ = 259.9882_2$ std. dev. = $\pm$ 0.0027 (10.1 ppm)

Calculated for $C_7H_{11}F_2I = 259.9873_6$

dev. = 0.0008_6 (+ 3.3 ppm)

260 (0.1) M^+

133 (71.3) M^+-I

128 (10.7)

127 (8.0)

113 (21.2)

97 (15.4)

91 (29.1)

85 (11.0)

83 (16.7) M^+-CF_2I

77 (26.3)

73 (33.2)

70 (13.4)

69 (22.0)

67 (16.7)

65 (28.8)

61 (14.1)

57 (35.4)

55 (37.5)

53 (17.8)

51 (11.1)

43 (32.0) C_3H_7

41 (100) C_3H_5

39 (46.3)

29 (13.6)

28 (15.2)

27 (20.9)

Photolysis of CF_2I_2 and 54 without Hg

In the absence of mercury, a photolysis performed as described above showed only 40% conversion of CF_2I_2 and gave a similar product ratio.

Gas Phase Photolysis of CF_2I_2 and 54

Into a 570 mL vycor photolysis bulb were vacuum transferred 0.74 mmol of CF_2I_2 and 2.1 mmol of 49. The system was thoroughly degassed and then the bulb was suspended in a Rayonet® photolysis apparatus equipped with 254 nm source lamps. Almost immediately the reaction mixture darkened with I_2 coloration. Photolysis was continued for 4h. All volatile material was vacuum transferred into a small plum-bottom flask and examined by ^{19}F NMR: 19% 46, 14% 45 and two unidentified products 6% ϕ103.9(s) and 2% ϕ96.2(s).

Photolysis of Neat CF_2I_2

Liquid CF_2I_2 was degassed and a sample was allowed to expand into an evacuated vycor photolysis bulb until its maximum vapor pressure at room temperature was obtained (28 torr). The bulb was closed off and the CF_2I_2 was photolyzed at 254 nm as described above. Within minutes, I_2 was seen crystallizing on the walls of the bulb. Afer 2h of photolysis, all volatile material was vacuum transferred to a small flask and examined by ^{19}F NMR which showed ICF_2CF_2I (57, ϕ53.2) and CF_2I_2 to be the only ^{19}F-containing species present in other than trace amounts. $57/CF_2I_2 \simeq 10/1$.

Photolysis of CF_2I_2 and 54 at Elevated Temperature

A solution of 0.79g of CF_2I_2 (2.56 mmol) and 0.81g of 54 (9.6 mmol) was refluxed and photolyzed for 21h under a blanket of dry N_2. A Sears 150W, 120V projector flood lamp was used as a light source mounted about 8 cm from the reaction flask. The ^{19}F NMR spectrum of the crude reaction mixture showed 56 to be the major ^{19}F-containing species in addition to small amounts of other unidentified products. No 55 or unreacted CF_2I_2 was observed.

Photolysis of CF_2I_2 with 54 and Aqueous NaOH

Into a 25 mL round-bottom flask were placed 0.56g of 54 (6.7 mmol), 15 mL CH_2Cl_2 1.16g of CF_2I_2 (3.82 mmol) and 5 mL of 5M aqueous NaOH. The magnetically stirred reaction flask was equipped with a reflux condenser and the mixture was photolyzed for 23h. The two-phase liquid system was separated and the organic phase was dried over $CaCl_2$ then distilled to remove most of the CH_2Cl_2. Absolute yields were not determined; however, ^{19}F NMR analysis showed four ^{19}F-containing species (two unidentified) in the following relative amounts: 54% 56, 30% 55, 9% ϕ80(s), 7% ϕ38(s).

Photolysis of CF_2I_2 with 1-Hexene and Hg

Into a small carius tube were weighed 0.36g of CF_2I_2 (1.2 mmol), 0.90g of 1-hexene (10.7 mmol) and 0.59g of mercury (2.9 mmol). The mixture was degassed and the tube was sealed under vacuum at -196°C. After thawing, the

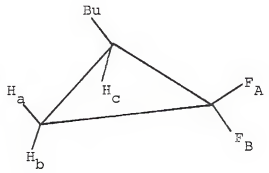
mixture was photolyzed and mechanically agitated for 18h. The tube was opened and the volatile material was examined by ^{19}F NMR. The reaction yield was too low to be determined by NMR integration. A trace amount of 1-butyl-2,2-difluorocyclopropane 60 was detected and identified by its Fourier transformed ^{19}F NMR spectrum.

AB quartet with further splitting

midpoint ϕ136.7, J_{AB}=156.3 Hz, $\Delta\phi$=16.8

$J(F_aH_a)$=12.4 Hz

$J(F_bH_b)-J(F_bH_c)$=13.5 Hz



60

Some trans, vicinal H-F couplings are also visible (1-3 Hz). The ^{19}F NMR spectrum of 60 closely resembled that of model compound 76.

76

Attempted Thermal Reaction of CF_2I_2 and 2,3-Dimethyl-2-butene 54.

Into a small Carius tube were placed 0.575g of CF_2I_2 (1.89 mmol), and 0.817g of 54 (9.73 mmol). The solution was degassed and the tube was sealed under vacuum at -196°. After it was allowed to warm to ambient temperature, the tube was placed in a preheated oil bath and kept at 83-87°C for 32h. Analysis by GC and NMR showed the only significant new component in the mixture was 2,3-dimethyl-1-butene which resulted from the I_2-catalyzed isomerization of 54.

Simmons-Smith Reactions of CF_2I_2

Reaction of CF_2I_2 with 54, Zn, and CuCl

The following procedure was patterned after that of Rawson and Harrison.[63] A 25-mL, three-necked flask was equipped with a spiral condenser, a rubber septum, an addition funnel, and two stopcocks for the inlet and outlet of N_2. A solution of 0.463g of CF_2I_2 (1.16 mmol) in 1 mL of anhydrous diethyl ether was placed into the addition funnel. Into the reaction flask were placed 0.219g of Zn dust (3.35 mmol), 0.322g of freshly prepared CuCl,[75] and 2 mL of anhydrous diethyl ether. The magnetically stirred mixture was warmed to gentle reflux for 15 minutes whereupon 0.5 mL of 54 (4.2 mmol, Aldrich) was added by syringe. Heating was temporarily discontinued while the CF_2I_2 solution was added dropwise over 10 minutes. Reflux heating was resumed for 4.5h. All volatile material was vacuum transferred to a small flask. Yield of 55 was 3% by ^{19}F NMR.

Reaction of CF_2I_2 and 54 with Zn and Ultrasound

Into a 10-mL flask were weighed 0.36g of Zn dust (5.5 mmol), 0.43g of 1,2-dimethoxyethane, and 0.56g of 54. The flask was equipped with a spiral condenser, nitrogen inlet and outlet stopcocks and an addition funnel containing a solution of 0.96g of CF_2I_2 (3.16 mmol) in 0.66g of 1,2-dimethoxyethane. The system was purged with a slow flow of dry N_2 and the reaction vessel was mounted inside a sonic cleaner (Bransonic 2 , 117V, 60 Hz, 40W, Branson Instruments Co.) at a depth that produced the maximum agitation. After 20 minutes of sonication, the CF_2I_2 solution was added dropwise over 6 minutes and the heterogeneous reaction mixture was sonicated for an additional 3 hours while the bath temperature climbed slowly to 58°C. All volatile material was vacuum transferred from the mixture and the clear, colorless solution was examined by ^{19}F NMR. Yield of 55 was 38%.

Free-Radical Additions of CF_2I_2 to Alkenes

Addition of CF_2I_2 to 1-Hexene

Into a 10-mL round-bottomed flask were weighed 0.325g of CF_2I_2 (1.07 mmol), 1.108g of 1-hexene (13.2 mmol), and 10mg of benzoyl peroxide. After refluxing the magnetically stirred solution for 10.5h, excess olefin was removed by rotary evaporation, and the pale pink residue was purified

by flash chromatography,[76] eluting with hexane, to yield 0.304g of 1,1-difluoro-1,3-diiodoheptane 6l; 73%.

^{1}H NMR: δ 0.95 (t, J=6 Hz, 3H)
δ 1.2 - 3.1 (br m, 6H)
δ 2.8 - 3.6 (m, 2H)
δ 4.32 (quint, J=7 H,1H)

^{19}F NMR: ϕ 36.18 (midpoint, AB, J_{AB}= 172 Hz, Δϕ=1.75)
downfield F (dd, J=18 Hz, J=10 Hz)
upfield F (dd, J=17 Hz, J=14 Hz)
Also visible was ∿3% of the opposite regioadduct
2-(difluoroiodomethyl)-1-iodohexane
ϕ 38.1 (midpoint AB of d, J_{AB}=172, Δϕ=1.75, J_{HF}=10 Hz)

^{13}C NMR: δ 99.6 (t, J=316 Hz, C_1)
δ 58.2 (t, J=40 Hz, C_2)
δ 39.2 (s)
δ 31.5 (s)
δ 25.3 (br s, C_3)
δ 21.7 (s)
δ 13.9 (s, C_7)

IR: 895(s), 1060, 1165, 2870, 2880, 2930(s), 2970(s)cm^{-1}

MS: 388 (1.0) M^+
261 (4.8) M^+-I
41 (100) C_3H_5
and many smaller fragments

Addition of CF_2I_2 to Methyl Propenoate

A mixture of 1.02g of methyl propenoate (11.8 mmol, MCB, freshly distilled from phenothiazene onto molecular sieves), 2.15g of CF_2I_2 (7.07 mmol), about 4 mL of benzene and 0.1g of benzoyl peroxide (0.1 mmol) was treated as described above for 19h at 90-106°C to yield 36% of unreacted CF_2I_2 and 1.29g of methyl 4,4-difluoro-2,4-diiodobutanoate 63 47%.

^{1}H NMR: δ 4.55 (dd, J=10 Hz, J=3.8 Hz, 1H)

δ 2.84 - 3.95 (m, 2H)

δ 3.77 (s, 3H)

^{19}F NMR:φ 40.1 (midpoint, AB, J_{AB}=176 Hz, Δφ=0.3, J_{HF}=15 Hz)

^{13}C NMR:δ 170.3 (s, C=O)

δ 97.0 (t, J=315 Hz, CF_2I)

δ 54.5 (t, J=21 Hz, CH_2)

δ 53.3 (s, CH_3)

δ 7.8 (t, J=2.4 Hz, CHI)

MS: 359 (1.3) M-OCH_3

331 (0.3) M-CO_2CH_3

263 (20.8) M-I

254 (0.8) I_2

136 (100)

127 (24.5) I

77 (27.7) $C_3H_3F_2$

64 (3.0) $C_2H_2F_2$

59 (17.3) CO_2CH_3

31 (13.9) OCH_3

and other fragments

No M^+ was observed.

Addition of CF_2I_2 to trans-4-Octene

A mixture of 0.70g of CF_2I_2 (2.3 mmol), 0.81g of trans-4-octene (7.2 mmol) and 0.10g of benzoyl peroxide was allowed to react as described above at 110° for 24h to yield 84% of a 1:1 mixture of the two possible diastereoisomeric 4-(difluoroiodomethyl)-5-iodooctanes 65. The ^{1}H-NMR of the reaction mixture shows the hydrogens on C_5 as multiplets δ4.45.

^{19}F NMR:ϕ 36.6 (midpoint, AB of d, $\Delta\phi$=3.02, J_{AB}=187 Hz)
downfield F (d, J_{HF}=14 Hz)
upfield F (d, J_{HF}=17.5 Hz)
ϕ 37.5 (midpoint, AB of d, $\Delta\phi$=3.17, J_{AB}=188 Hz
downfield F (d, J_{HF}=13.5 Hz)
upfield F (d, J_{HF}=15 Hz)

Radical Addition of CF_2I_2 to Cyclohexene

A mixture of 1.00g of CF_2I_2 (3.3 mmol), 1.20g of cyclohexene (14.6 mmol), and 0.03g of benzoyl peroxide (0.1 mmol) was allowed to react at 90-97°C for 20h to yield 61% of a mixture consisting of 65% trans-1-(difluoroiodomethyl)-2-iodocyclohexane 67, 28% cis-1-(difluoroiodomethyl)-2-iodocyclohexane 68, 4% unreacted CF_2I_2, and 3% of an unidentified product (ϕ42, midpoint, AB J≈10 Hz,

$\Delta\phi \simeq 1$ ppm). The major diastereomeric products were isolated by preparative GLC. The column was 20% OV-210 on Chromasorb WHP 60/80, 10' x 0.25", at 150°C. Some slight decomposition was noted under these GC conditions. The retention times were trans = 27 min, and cis = 33 min.

67

^{19}F NMR: ϕ 34.5 (d, J=10.3 Hz)

^{1}H NMR: δ 4.27 (ddd, J=8.5 Hz, J=7.0 Hz, J=4.5 Hz, 1H, H-CI)

δ 1.1 - 2.5 (m, 9H)

^{13}C NMR: δ 108 (t, J=319 Hz, CF_2I)

δ 57.3 (t, J=16.5 Hz, C_1)

δ 38.3 (s)

δ 27.9 (s)

δ 27.5 (dd, J=3.6 Hz, J=2.5 Hz)

δ 26.2 (s)

δ 22.7 (s)

68

^{19}F NMR: ϕ 42.4 (midpoint, AB, J_{AB}=172 Hz, $\Delta\phi$=5.12)

downfield F (d, J_{HF}=13.6 Hz)

upfield F (d, J_{HF}=12.8 Hz)

^{1}H NMR: δ 4.75 (br s, 1H, H-CI)

δ 1.1 - 2.3 (m, 9H)

^{13}C NMR: δ 105.7 (dd, J=321 Hz, J=320 Hz, CF_2I)

δ 57.5 (t, J=9.8 Hz, C_1)

δ 37.2 (s)

δ 32.1 (dd, J=3.7 Hz, J=2.4 Hz, C_6)

δ 24.8 (s)

δ 23.6 (t, J=2.4 Hz, C_2)

δ 22.2 (s)

Addition of CF_2I_2 to 2,3-Dimethyl-2-butene 54

Refluxing 0.56g of CF_2I_2 (1.8 mmol), 0.86g of 54 (10 mmol), and 0.02g of benzoyl peroxide (0.08 mmol) for 24h gave 56 as the only F-containing product. More than half of the CF_2I_2 was recovered unchanged. The yield was 95% based on converted CF_2I_2 and ^{19}F NMR integration.

Zinc Reductions of 1,1-Difluoro-1,3-diiodoheptane 61

Into a 10-mL flask were placed 0.180g of 61 (0.464 mmol), 1 mL of THF (freshly distilled from $LiAlH_4$ and storred over CaH_2 until use), 0.083g of Zn dust (1.28 mmol, acid washed) and a small crystal of $ZnCl_2$. The magnetically stirred mixture was refluxed for 8.5 h. All volatile material was then vacuum transferred and analyzed by ^{19}F NMR. The relative yields of F-containing products were 52% 59, 25% 60 and 23% of other mostly unidentified products. When a similar reaction was carried out in ethanol, the relative yields were 36, 23 and 41% respectively. The ^{19}F NMR spectrum of 60 was identical to that reported above for 60 prepared from photolysis of CF_2I_2 with 1-hexene.

59

^{19}F NMR:ϕ 116.1 (dt, J=57 Hz, J=17 Hz)

CHAPTER 6
GENERAL CONCLUSIONS

The thermal rearrangement of 1,1-difluorospiropentane to 2,2-difluoromethylenecyclobutane was shown to proceed via two competing mechanisms. Initial C_1-C_2 bond cleavage is three times faster than initial C_4-C_5 bond cleavage.

The kinetics for the thermal isomerization of cis,cis-1-fluoro-2-methyl-3-vinylcyclopropane indicate that a cis-monofluoro substituent in the 1 position lowers the activation energy for the 1,5-homodienyl hydrogen shift by 3.3 kcal/mol relative to the hydrocarbon. This value is less than half of the E_a lowering observed for the rearrangement of the gem-difluoro species.

Difluorodiiodomethane is now available in practical quantities through the treatment of CI_4 with HgF_2. This versatile reagent has been used in photochemical and Simmons-Smith cyclopropanations and undergoes facile free-radical additions to alkenes.

APPENDIX A
KINETIC DATA

Table A-1. Kinetic Data for Thermolysis of 12 at 339.6°C.

min	% 12	% 13	% std
1.9	38.14	-	61.50
1.9	38.36	-	61.64
1.9	39.19	-	61.37
26.2	37.13	1.54	61.02
26.2	37.20	1.50	60.80
26.2	37.28	1.35	60.81
52.6	34.28	2.93	62.32
52.6	34.14	2.90	62.22
52.6	34.75	3.03	61.78
52.6	34.48	3.01	61.71
52.6	34.40	2.98	62.13
81.7	32.48	4.68	62.26
81.7	32.09	4.62	61.63
81.7	32.25	4.47	62.27
81.7	32.21	4.51	62.45
163.7	27.31	8.22	62.86
163.7	27.52	8.33	63.21
163.7	27.36	8.33	63.10
163.7	27.50	8.28	63.20
201.7	24.98	9.73	63.41
201.7	25.20	9.76	63.38
201.7	25.09	9.89	63.41
201.7	25.26	9.90	63.52
244.5	23.60	11.47	63.75
244.5	23.29	11.29	64.20
244.5	22.53	11.32	64.06
244.5	23.37	11.34	64.40

Table A-2. Kinetic Data for Thermolysis of 19 at 339.6°C.

min	% 19	% 23+24+27	% std
1.5	32.15	-	67.20
1.5	32.92	-	67.08
1.5	32.42	-	67.58
1.5	32.68	-	66.62
20.6	31.70	0.76	67.54
20.6	31.37	0.68	67.95
20.6	31.56	0.77	67.50
62.3	28.73	2.55	67.96
62.3	28.37	2.49	68.66
62.3	29.04	2.41	68.06
92.4	26.63	3.78	68.24
92.4	27.21	3.78	67.94
92.4	27.09	3.73	68.62
128.1	25.99	4.71	68.38
128.1	26.09	4.67	68.11
128.1	25.70	4.54	67.95
168.0	23.57	6.37	69.43
168.0	23.58	6.40	68.58
168.0	23.91	6.40	68.74
168.0	23.18	6.38	69.22
263.4	19.72	8.67	70.67
263.4	19.62	8.88	70.51
263.4	20.04	8.95	70.09

Table A-3. Kinetic Data for Thermolysis of 31 at 152.8°C.

min	% 31	% P_1	% P_2	% P_3	% P_4	% std
0	92.912	0.631	0.649	0.025	0.022	3.450
0	92.886	0.623	0.632	0.018	0.008	3.450
0	92.840	0.609	0.584	-	-	3.462
15	84.579	7.758	0.852	1.231	0.098	3.381
15	84.558	7.684	0.858	1.211	0.101	3.372
15	84.125	7.563	0.944	1.243	0.140	3.401
30	75.877	14.719	1.086	2.362	0.204	3.465
30	76.203	14.722	1.173	2.348	0.195	3.392
30	75.604	14.475	1.290	2.260	0.206	3.436
45	72.896	15.576	2.564	2.359	0.260	3.660
45	72.973	15.350	2.728	2.246	0.225	3.685
45	73.002	15.082	2.875	2.190	0.168	3.755
60	62.364	25.782	1.791	3.867	0.381	3.463
60	62.489	25.574	1.808	3.859	0.324	3.507
60	62.523	25.521	1.867	3.921	0.411	3.499
75	59.008	26.651	3.097	4.262	0.503	3.707
75	58.964	26.294	3.166	4.193	0.489	3.702
75	58.865	26.008	3.331	3.970	0.576	3.726
105	45.212	39.386	2.596	6.109	0.601	3.483
105	45.191	39.231	2.522	6.190	0.587	3.470
105	45.024	38.977	2.593	5.864	0.300	3.471

Table A-4. Kinetic Data for Thermolysis of 31 at 157.1°C.

min	% 31	% P_1	% P_2	% P_3	% P_4	% std
12	82.833	7.533	1.007	1.260	0.182	4.091
12	81.955	7.828	1.195	1.407	0.249	4.120
12	80.591	7.820	1.497	1.459	-	4.267
24	73.921	13.644	1.425	2.503	-	4.137
24	73.571	14.576	1.462	2.411	0.155	4.060
24	73.360	14.448	1.437	2.448	0.250	4.096
36	65.692	20.788	1.757	3.772	0.441	4.184
36	65.491	20.649	1.692	3.698	0.342	4.192
36	65.397	20.580	1.901	2.867	-	4.326
48	59.569	26.269	1.945	4.462	0.327	4.206
48	59.183	25.929	1.967	4.506	0.364	4.285
48	59.538	26.124	1.841	4.416	0.296	4.258
60	58.565	23.186	5.230	3.602	0.629	4.826
60	57.992	23.120	5.124	3.463	0.460	4.925
60	59.150	23.133	5.527	3.557	0.488	4.944
72	51.575	27.697	6.454	4.088	0.498	4.857
72	51.966	27.355	6.691	3.878	-	4.881
72	50.668	26.622	6.655	3.407	-	4.875
84	50.384	25.713	9.131	2.825	-	5.401
84	50.499	25.678	9.340	2.858	0.559	5.297
84	50.753	25.520	9.393	2.737	0.444	5.275

Table A-5. Kinetic Data for Thermolysis of 31 at 160.4°C.

min	% 31	% P_1	% P_2	% P_3	% P_4	% std
12	82.488	8.035	1.024	1.285	0.161	3.497
12	81.933	8.916	0.910	1.636	0.154	3.527
12	80.792	9.036	1.040	1.619	0.194	3.502
24	71.607	17.309	1.193	3.392	0.285	3.540
24	71.692	17.361	1.239	3.165	0.224	3.407
24	69.705	18.119	1.558	3.595	0.387	3.471
36	61.706	24.930	1.545	4.783	0.325	3.682
36	61.064	25.219	1.705	4.872	0.364	3.625
36	59.324	24.671	2.810	4.901	0.204	3.791
48	53.727	31.876	1.717	6.016	0.406	3.597
48	53.468	31.864	1.738	5.873	0.400	3.624
48	53.917	30.252	1.534	5.630	0.290	3.575
60	47.610	34.869	4.201	5.529	0.440	3.919
60	47.696	34.217	4.359	5.881	0.677	3.985
60	47.465	33.603	4.745	5.593	-	3.981
72	41.384	39.436	4.668	6.799	0.525	4.027
72	41.602	38.946	4.875	6.596	0.413	4.079
72	41.419	38.807	4.921	6.589	0.443	4.065
84	37.006	40.828	5.960	6.297	0.869	4.135
84	37.270	41.411	6.481	5.247	0.568	4.060
96	30.425	38.070	6.168	7.634	1.688	4.489
96	33.201	42.000	7.294	6.822	0.620	4.523
96	32.804	42.476	7.093	6.439	0.456	4.338
108	26.449	49.378	5.506	7.928	0.973	4.543
108	26.262	49.350	5.805	7.300	0.818	4.692
108	25.699	47.412	6.109	6.451	-	4.886

Table A-6. Kinetic Data for Thermolysis of 31 at 165.1°C.

0	% 31	% P_1	% P_2	% P_3	% P_4	% std
0	88.060	0.269	0.415	0.024	-	3.428
0	88.116	0.264	0.403	-	-	3.347
0	87.818	0.224	0.416	-	-	3.416
12	81.308	7.394	0.709	1.271	0.075	3.303
12	79.480	8.832	0.811	1.743	0.123	3.266
12	78.429	9.363	0.837	1.920	0.088	3.219
24	67.515	17.475	1.019	3.554	0.189	3.303
24	67.814	17.748	1.033	3.644	0.208	3.219
24	67.420	18.197	1.061	3.827	0.219	3.218
36	55.535	26.094	1.197	5.276	0.222	3.335
36	55.248	26.433	1.254	5.235	0.226	3.363
36	55.366	26.497	1.293	5.363	0.236	3.352
48	47.417	33.876	1.411	6.238	0.259	3.299
48	48.015	33.770	1.404	6.212	0.138	3.334
48	48.430	33.381	1.341	6.123	0.272	3.329
60	35.225	43.324	2.305	7.819	0.230	3.363
60	34.731	43.342	2.460	7.706	0.323	3.365
60	33.894	43.079	2.833	7.757	0.448	3.369
72	29.255	47.111	1.929	8.974	0.348	3.363
72	28.465	47.243	2.115	9.048	0.343	3.365
72	29.618	46.516	1.835	8.736	0.310	3.365
84	24.092	53.219	2.125	9.133	-	3.366
84	23.306	53.008	2.222	9.368	0.455	3.320
84	22.743	53.440	2.355	9.166	0.404	3.432

Table A-7. Kinetic Data for Thermolysis of 31 at 168.1°C.

min	% 31	% P_1	% P_2	% P_3	% P_4	% std
0	88.964	-	0.665	-	-	3.313
0	88.071	-	0.512	-	-	3.301
0	88.933	-	0.464	-	-	3.270
9	75.508	9.631	0.965	2.095	0.011	3.308
9	75.875	9.027	0.906	1.989	0.145	3.294
9	69.576	9.257	1.025	1.690	-	3.149
16	66.982	15.312	1.078	3.466	0.177	3.403
16	65.785	15.758	1.063	3.701	0.245	3.363
16	65.144	15.487	1.168	3.548	0.070	3.367
23	61.783	22.229	1.353	4.129	0.188	3.311
23	60.063	23.220	1.429	4.292	-	3.342
23	58.970	22.160	1.401	4.085	-	3.332
30	52.602	28.602	1.542	5.588	0.368	3.307
30	51.170	29.521	1.695	5.423	-	3.328
30	49.866	28.823	1.688	5.547	0.273	3.346
44	40.272	36.334	1.583	6.242	-	3.519
44	38.176	35.514	1.673	5.915	-	3.948
44	38.026	38.912	2.090	7.183	-	3.474
51	33.621	41.986	1.924	7.988	0.530	3.407
51	34.197	39.021	1.569	6.044	-	3.598
51	33.609	37.780	1.538	6.254	-	4.013

Table A-8. Kinetic Data for Thermolysis of 31 at 171.4°C.

min	% 31	% P_1	% P_2	% P_3	% P_4	% std
0	88.677	-	0.660	-	-	3.303
0	89.460	0.028	0.543	-	-	3.209
0	88.301	-	0.471	-	-	3.287
0	88.480	-	0.442	-	-	3.289
9	69.703	14.457	1.065	2.870	0.197	3.265
9	69.156	14.133	1.075	2.686	0.004	3.333
9	68.562	13.870	1.049	2.741	-	3.314
16	56.957	23.944	1.150	4.681	0.124	3.374
16	56.005	24.143	1.261	4.844	-	3.387
16	57.360	24.476	1.234	4.871	-	3.366
23	46.953	34.001	1.524	5.903	0.301	3.344
23	47.109	34.559	1.566	5.629	0.234	3.310
23	44.723	32.771	1.709	6.193	0.774	3.355
30	37.701	41.627	1.782	7.156	-	3.364
30	37.433	41.224	1.747	7.088	0.315	3.342
30	36.650	40.605	1.899	7.088	-	3.378
37	30.228	45.982	1.919	8.422	0.401	3.365
44	24.931	50.700	1.931	9.086	0.633	3.376
44	24.151	51.143	2.275	8.705	0.517	3.434
44	24.190	50.281	2.179	9.089	0.587	3.376
51	19.299	54.905	2.363	9.539	-	3.692
51	19.058	53.997	2.244	9.490	0.549	3.410
51	18.991	53.362	2.392	9.449	0.522	3.371

Table A-9. Kinetic Data for Thermolysis of 34 at 175.2°C.

min	% 34	% 43	% 44
0	96.9	0.1	0.5
0	96.9	0.1	0.5
24	88.67	2.91	3.23
24	85.35	4.41	1.30
24	87.39	3.70	0.89
24	84.93	1.86	1.26
48	77.77	9.41	9.45
48	72.24	10.80	5.07
48	86.16	8.57	5.27
48	81.69	8.00	5.93
73	63.59	14.16	10.44
73	71.17	16.42	10.38
73	65.80	13.65	8.88
73	68.63	18.67	3.3
73	64.56	16.83	5.60
97	54.03	18.39	14.95
97	55.71	18.34	8.99
97	51.51	14.04	3.59
97	50.75	15.08	2.82
125	53.31	20.33	14.37
125	55.96	24.79	15.62
125	46.90	23.85	16.9
151	47.04	26.73	15.77
151	47.43	24.21	19.80
151	47.28	24.59	16.67

Table A-10. Kinetic Data for Thermolysis of 34 at 181.0°C.

min	% 34	% 43	% 44	% std
23	15.84	1.47	1.26	79.48
23	15.08	1.52	1.26	80.29
23	14.24	1.59	1.20	81.36
49	13.04	2.82	2.01	79.39
49	12.27	2.94	1.86	81.13
49	12.49	3.37	1.90	80.01
71	12.22	4.20	2.84	78.09
71	13.03	4.05	3.12	78.40
71	11.40	4.58	2.76	78.64
99	9.58	5.48	3.46	79.71
99	6.91	6.44	3.62	80.63
99	8.71	5.10	3.13	80.37
132	7.26	7.17	4.22	79.33

Table A-11. Kinetic Data for Thermolysis of 34 at 190.0°C.

min	% 34	% 43	% 44
0	93.6	0.21	0.68
0	92.8	0.13	0.54
0	95.7	-	0.82
0	66.6	-	0.47
32	72.0	15.8	11.1
32	72.7	15.3	11.0
32	72.4	15.8	10.7
49	58.1	26.4	13.6
49	59.5	24.6	13.0
49	59.8	24.8	13.1
66	50.0	28.6	19.2
66	46.4	29.9	17.4
66	50.6	29.1	17.3
85	36.9	37.0	22.0
85	38.9	35.3	21.7
85	39.6	36.7	21.1
118	20.1	27.7	16.0
118	25.9	38.4	20.8
118	23.6	37.6	20.6
118	24.2	40.4	20.8

Table A-12. Kinetic Data for Thermolysis of 35 at 173.8°C.

min	% 35	% 43	% 44
0	52.75	7.97	3.93
0	47.88	7.78	1.55
0	53.87	9.01	3.09
0	50.24	9.17	1.72
60	62.17	8.26	3.53
60	57.98	9.50	5.67
60	54.76	9.79	4.96
91	54.79	9.89	7.34
91	55.29	9.68	7.52
91	59.66	8.51	7.39
91	56.37	13.42	7.31
251	44.93	19.70	12.33
251	43.00	16.53	9.43
251	41.65	16.21	9.80
468	33.20	22.63	18.26
468	37.11	22.92	17.88
468	31.67	24.30	13.10
660	29.34	26.99	23.31
660	26.56	30.28	16.44
660	29.15	27.21	17.35
660	20.50	22.70	11.82
1179	15.06	35.30	23.50
1179	14.75	32.18	13.58
1179	12.47	39.51	8.92

APPENDIX B
SELECTED SPECTRA

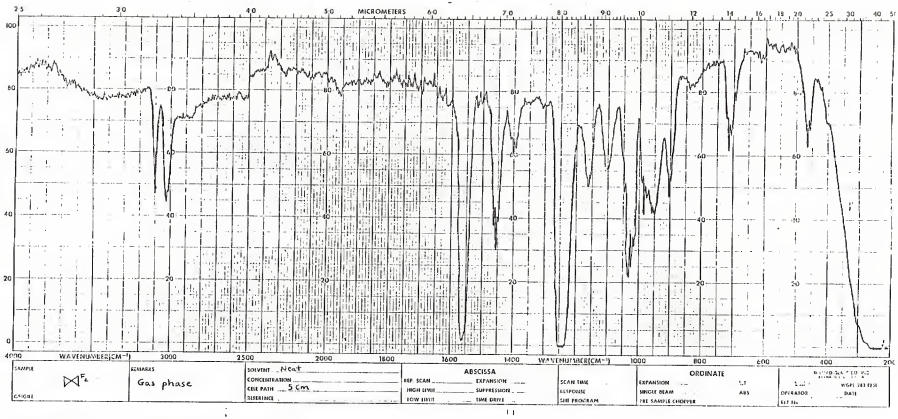


Figure B-1. IR Spectrum of 12.

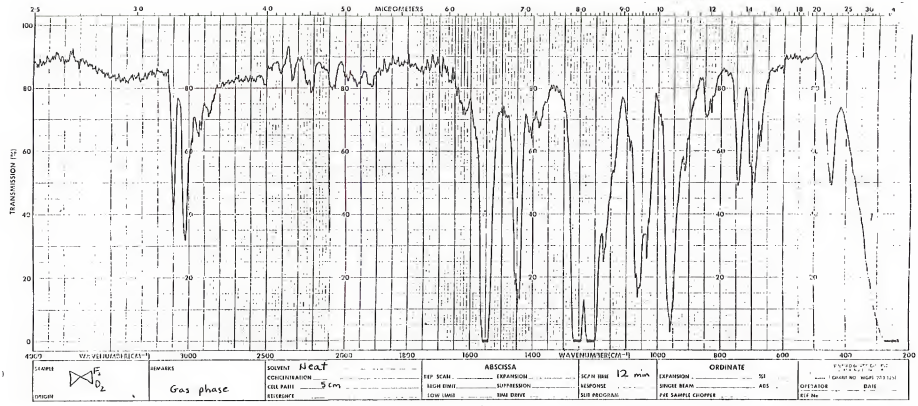


Figure B-2. IR Spectrum of 19.

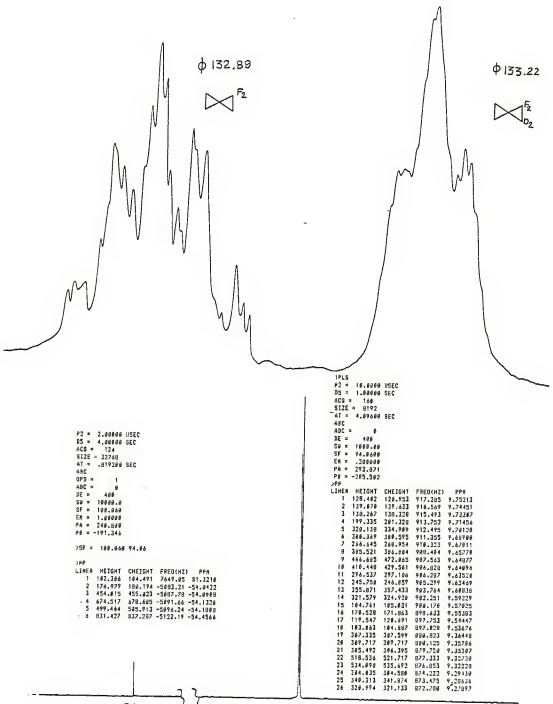


Figure B-3. ^{19}F NMR Spectrum of an ~50/50 Mixture of 12 and 19.

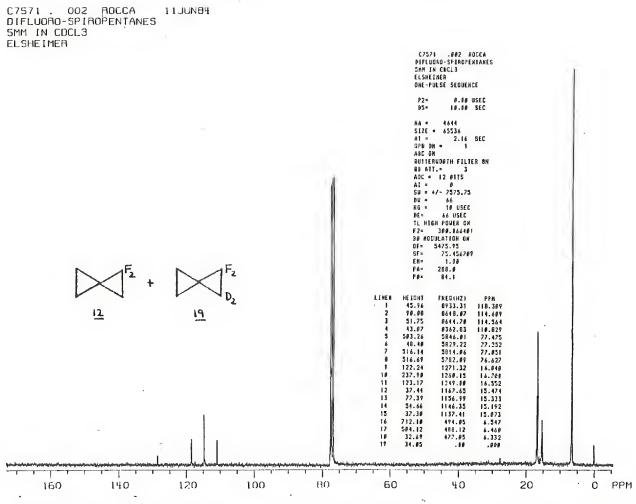


Figure B-4. ^{13}C NMR Spectrum of an ∿50/50 Mixture of 12 and 19, (Note: See also expansion, Figure B-5).

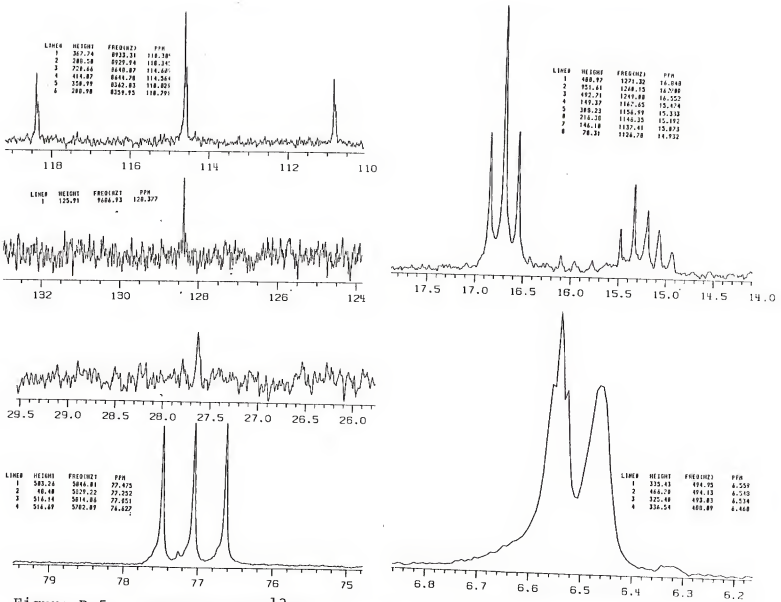


Figure B-5. Expansions of ^{13}C NMR Spectrum of an ∿50/50 Mixture of 12 and 19.

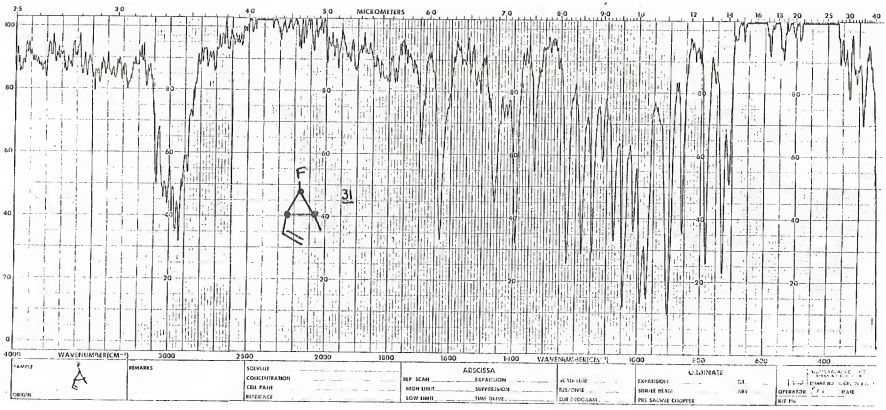


Figure B-6. IR Spectrum of 31.

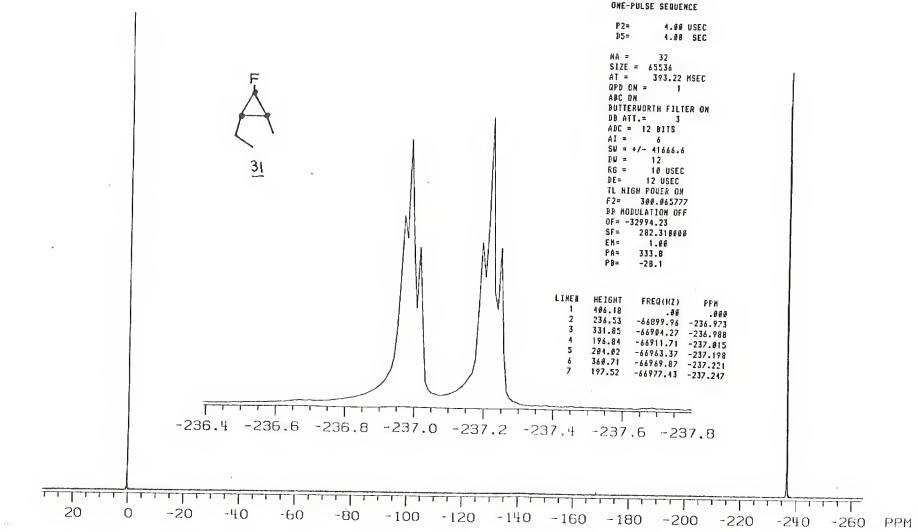


Figure B-7. ^{19}F NMR Spectrum of 31.

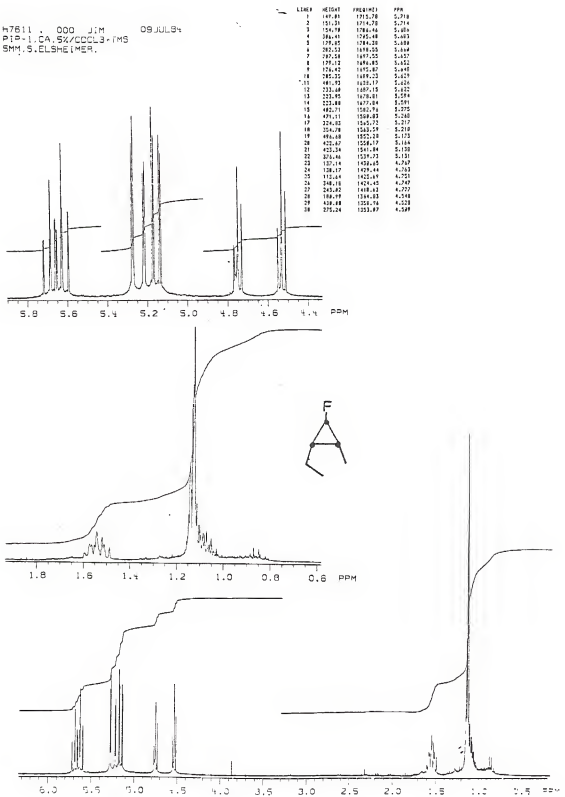


Figure B-8. ^{1}H NMR Spectrum of 31.

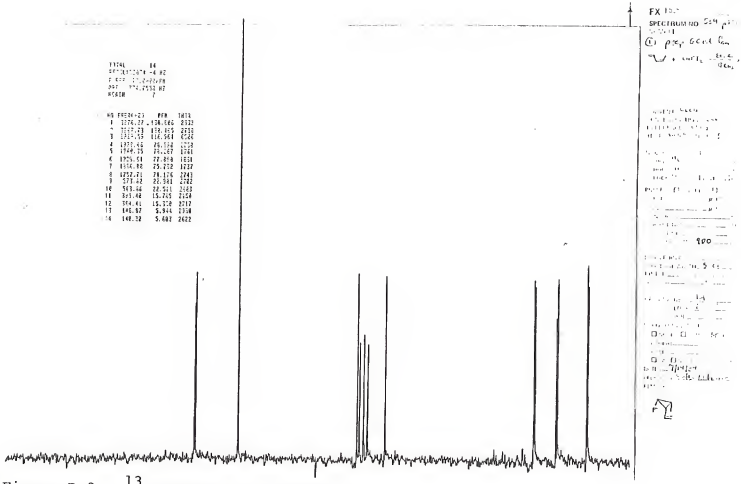


Figure B-9. ^{13}C NMR Spectrum of 31.

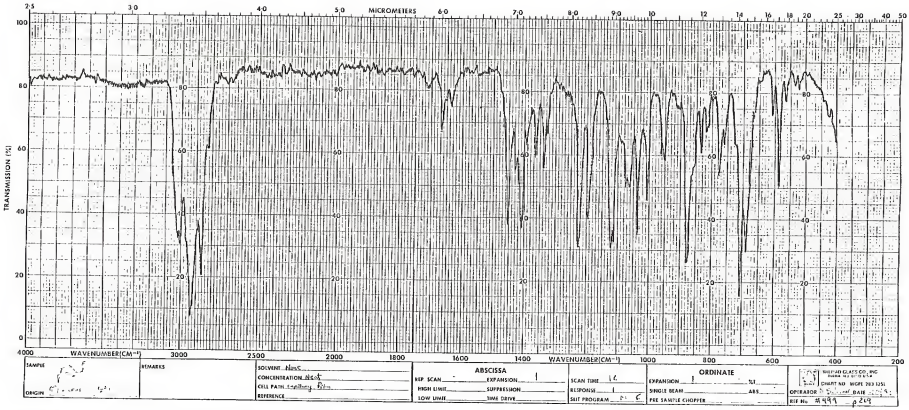


Figure B-10. IR Spectrum of 34.

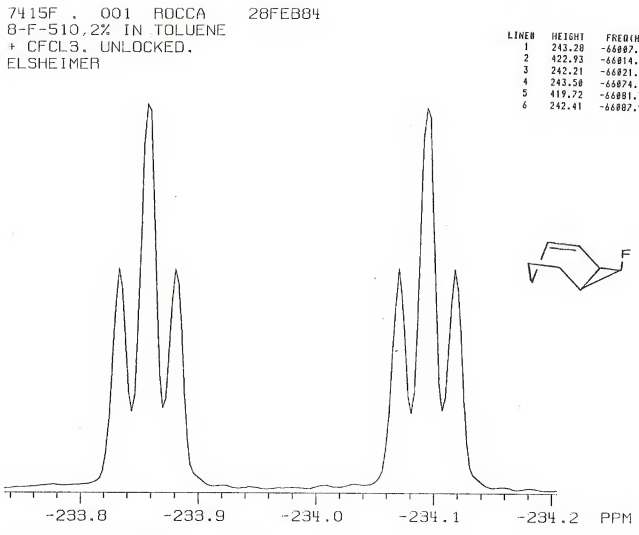


Figure B-11. ^{19}F NMR Spectrum of 34.

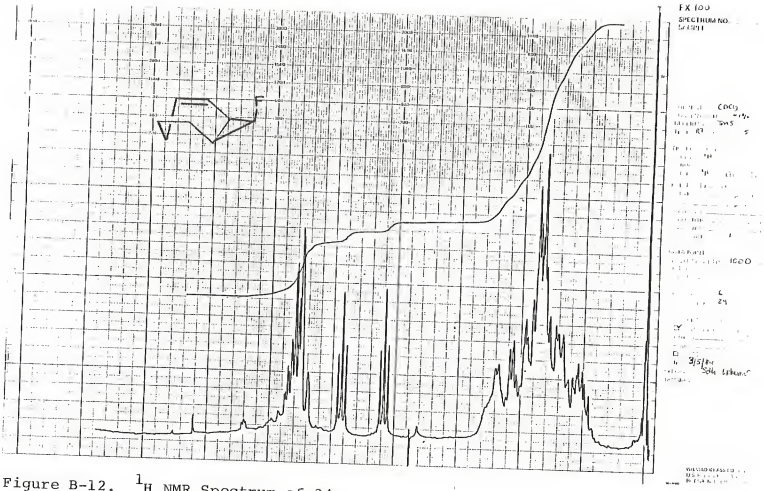


Figure B-12. ^{1}H NMR Spectrum of 34.

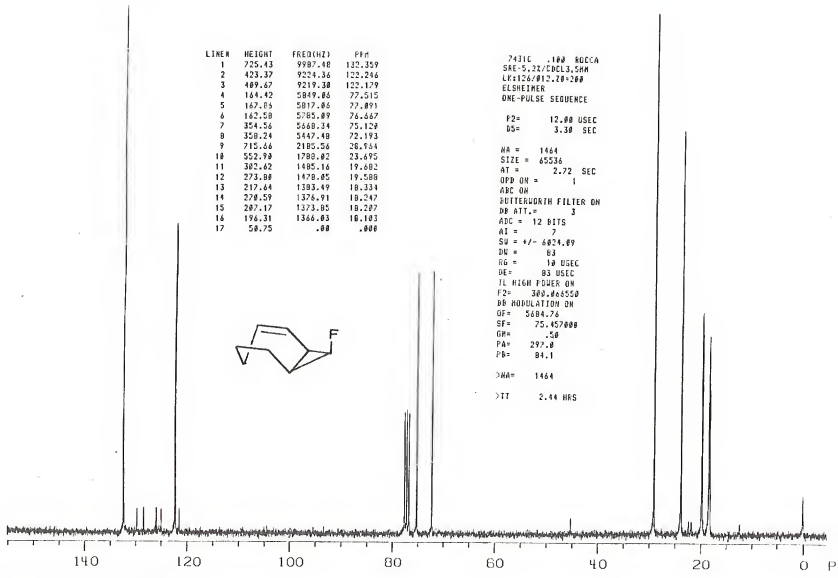


Figure B-13. ^{13}C NMR Spectrum of 34.

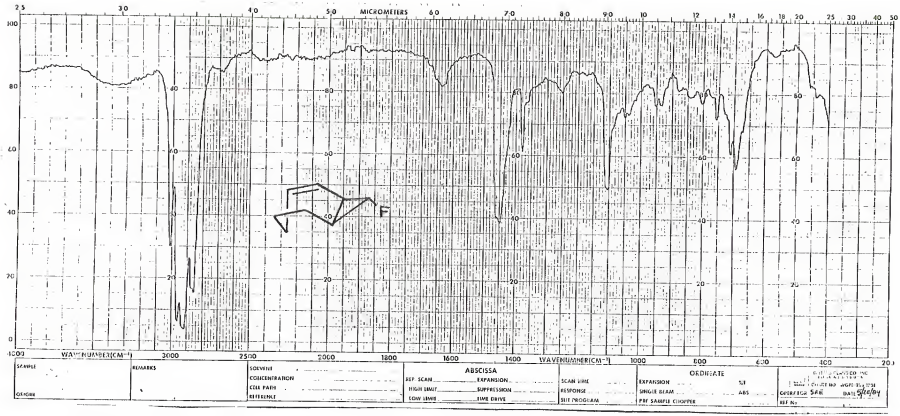
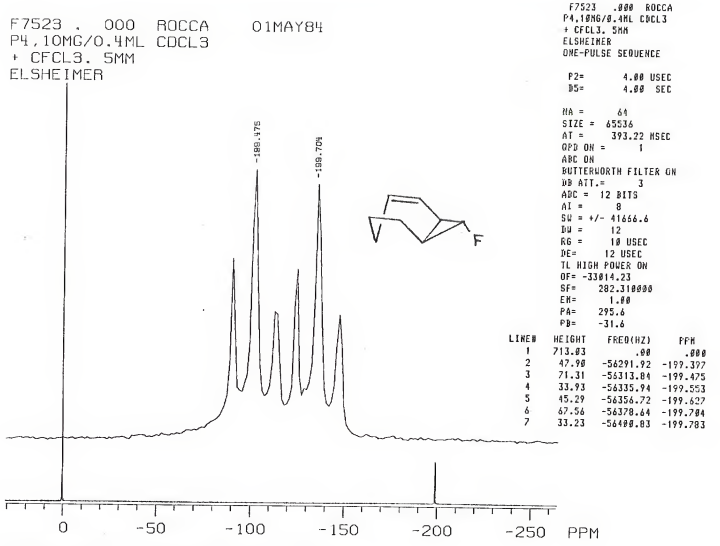


Figure B-14. IR Spectrum of 35.



F7523 .000 ROCCA
P4,10MG/0.4ML CDCL3
+ CFCL3. 5MM
ELSHEIMER
ONE-PULSE SEQUENCE

P2= 4.00 USEC
D5= 4.00 SEC

NA = 64
SIZE = 65536
AT = 393.22 MSEC
OBO ON = 1
ABC ON
BUTTERWORTH FILTER ON
DB ATT.= 3
ADC = 12 BITS
AI = 8
SW = +/- 41666.6
DW = 12
RG = 10 USEC
DE= 12 USEC
TL HIGH POWER ON
OF= -33014.23
SF= 282.310000
EN= 1.00
PA= 295.6
PB= -31.6

LINE#	HEIGHT	FREQ(HZ)	PPM
1	713.03	.00	.000
2	47.90	-56291.92	-199.397
3	71.31	-56313.84	-199.475
4	33.93	-56335.94	-199.553
5	45.29	-56354.72	-199.627
6	67.56	-56370.44	-199.704
7	33.23	-56400.83	-199.783

Figure B-15. ^{19}F NMR Spectrum of 35.

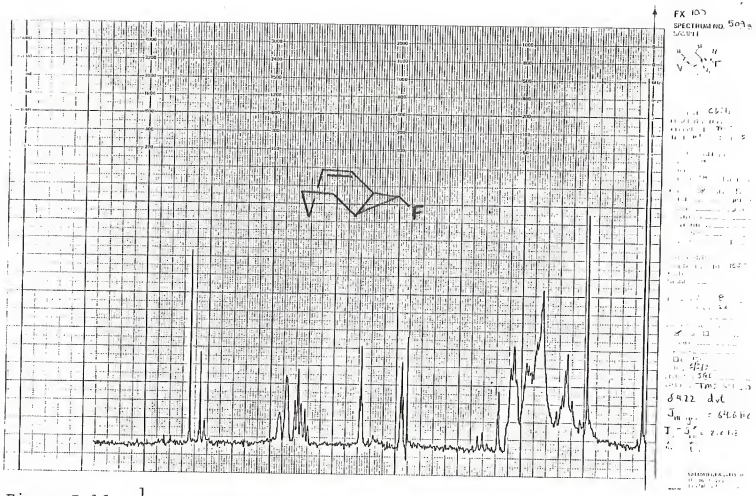


Figure B-16. ^{1}H NMR Spectrum of 35.

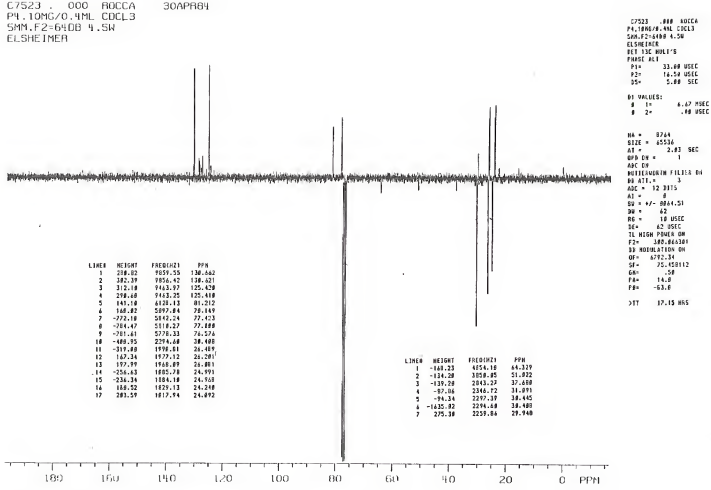


Figure B-17. ^{13}C NMR Spectrum of 35.

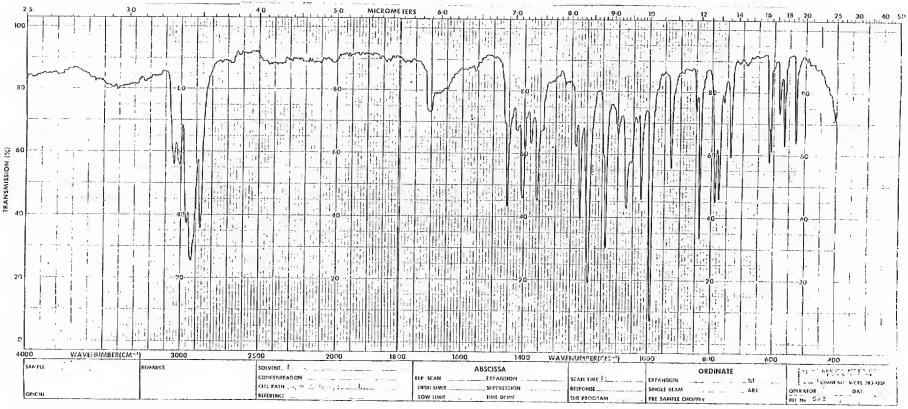


Figure B-18. IR Spectrum of 39.

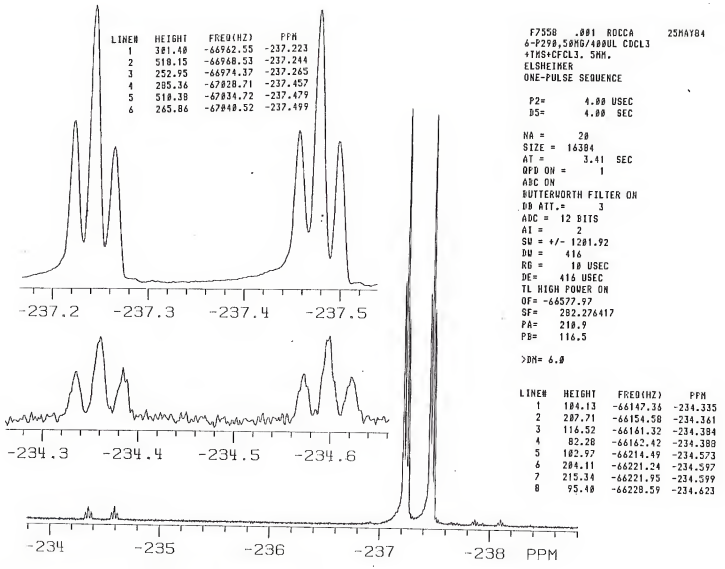


Figure B-19. ^{19}F NMR Spectrum of 39.

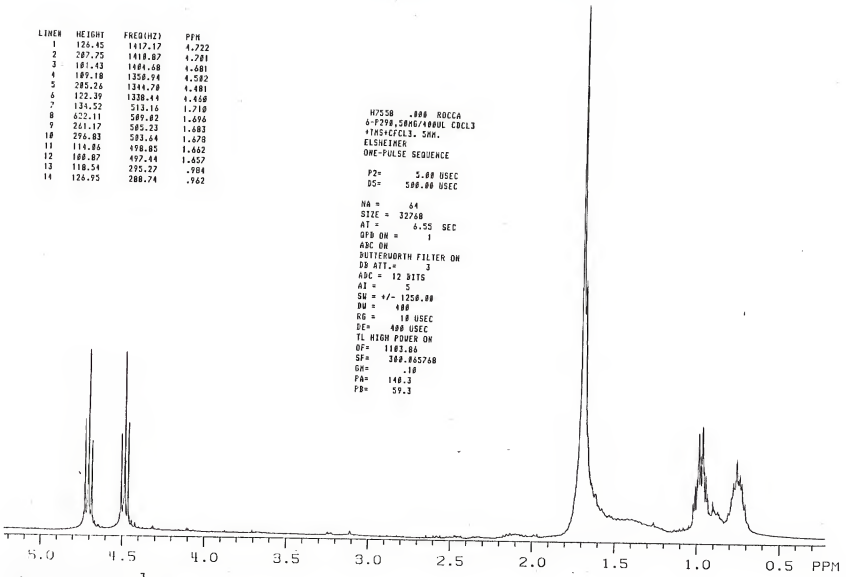


Figure B-20. ^{1}H NMR Spectrum of 39.

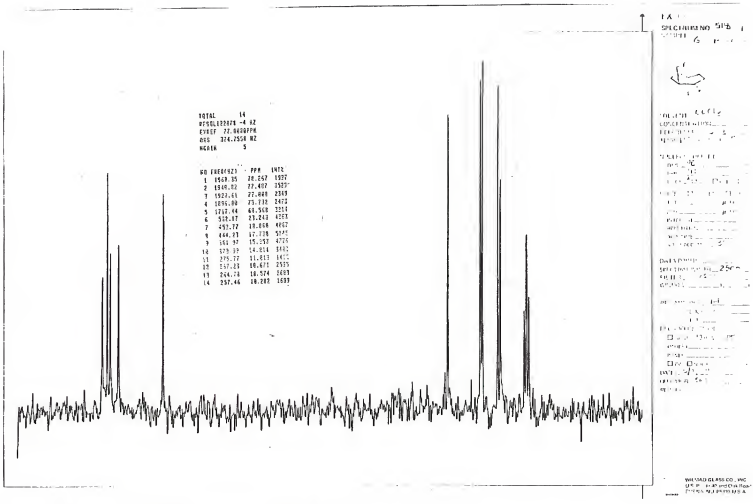


Figure B-21. ^{13}C NMR Spectrum of 39.

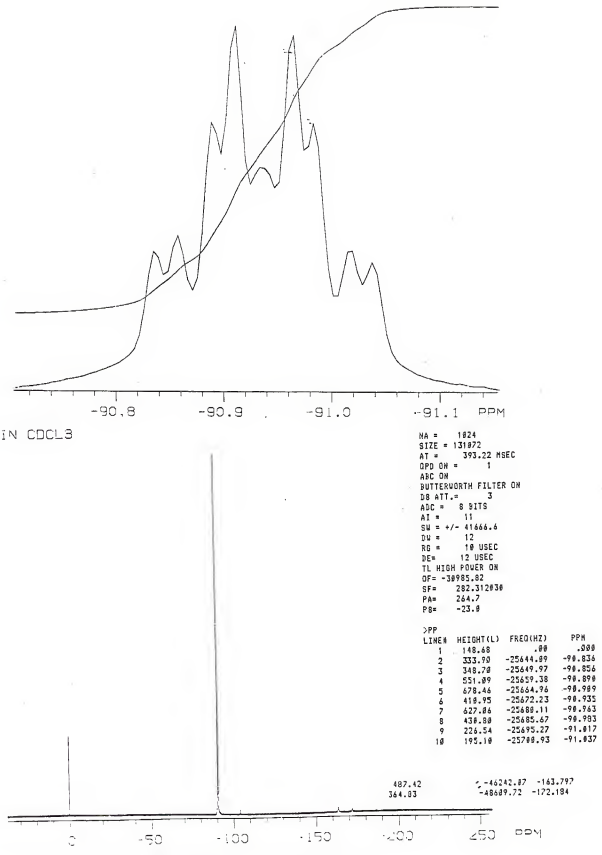


Figure B-22. ^{19}F NMR Spectrum of 43.

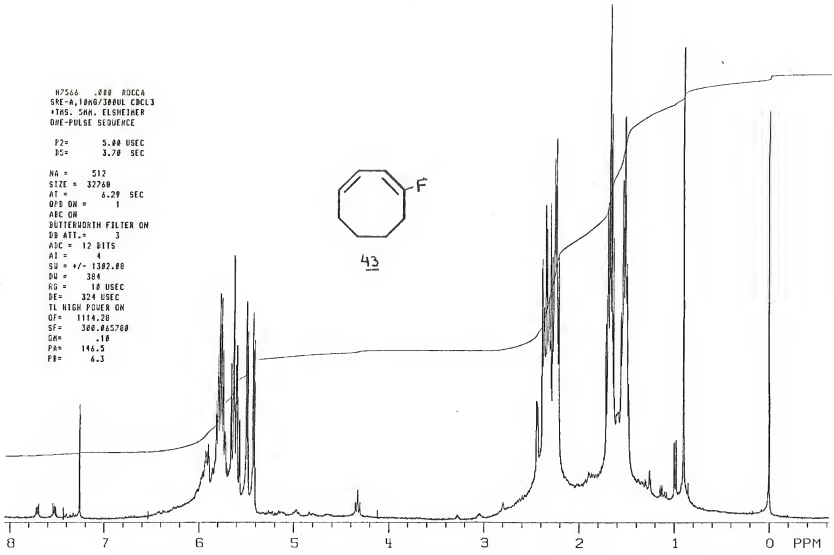


Figure B-23. ^{1}H NMR Spectrum of 43. (Note: See also expansions, Figure B-24).

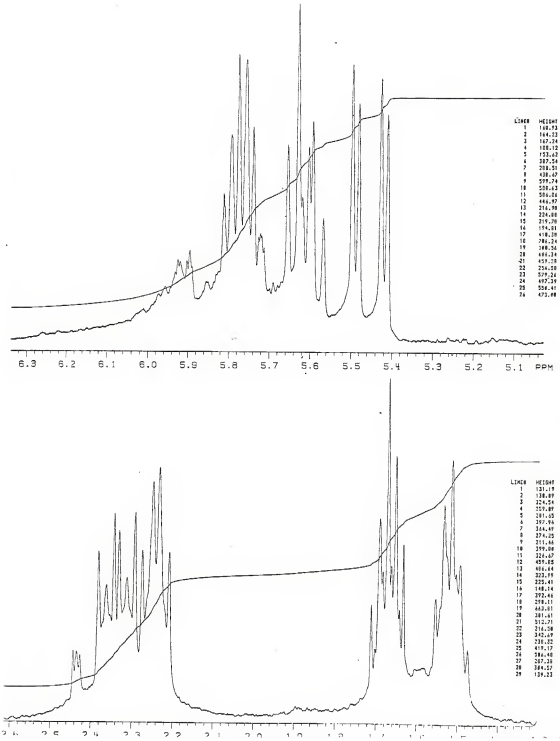


Figure B-24. Expansions of ^{1}H NMR Spectrum of 43.

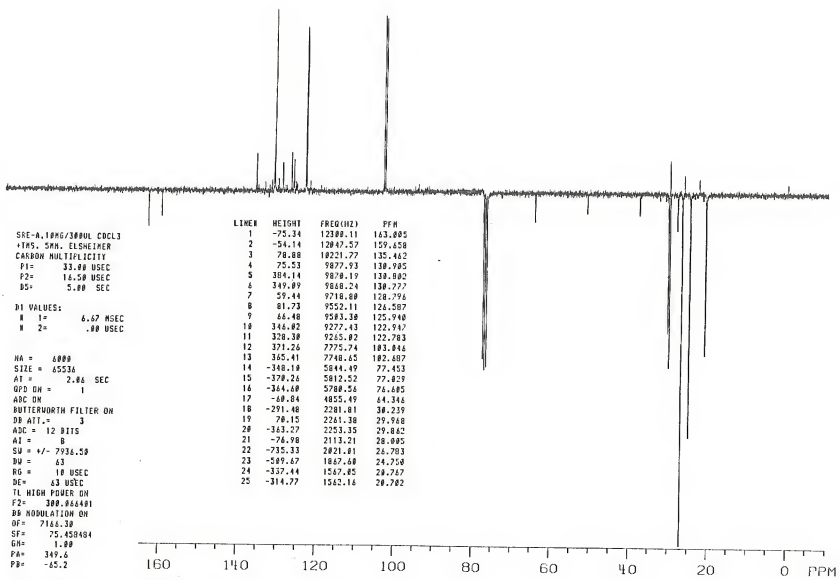


Figure B-25. ^{13}C NMR Spectrum of 43.

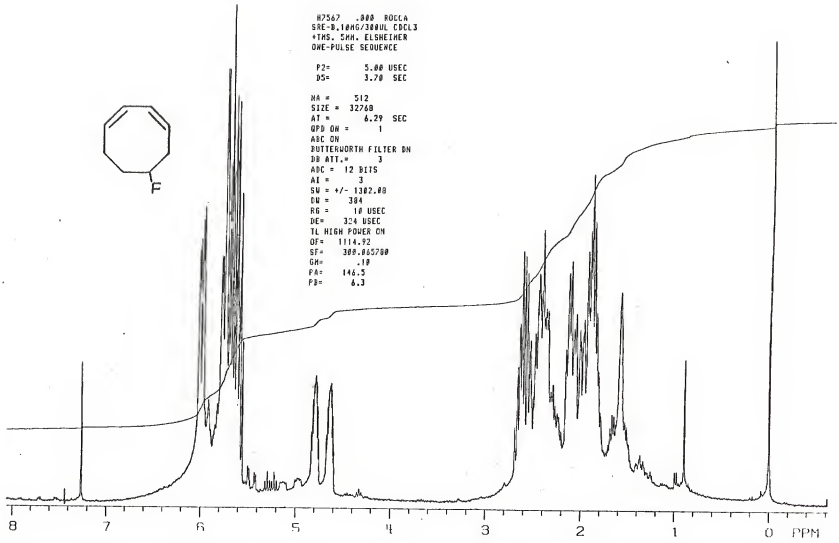


Figure B-26. ^{1}H NMR Spectrum of 44. (Note: See also expansions, Figure B-27.)

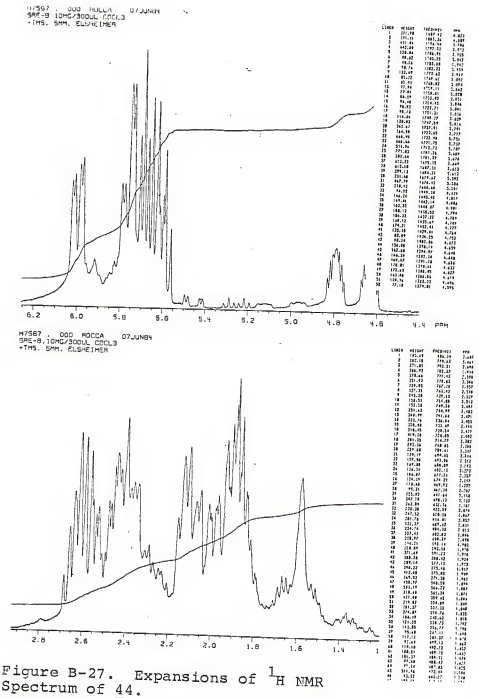


Figure B-27. Expansions of ^{1}H NMR Spectrum of 44.

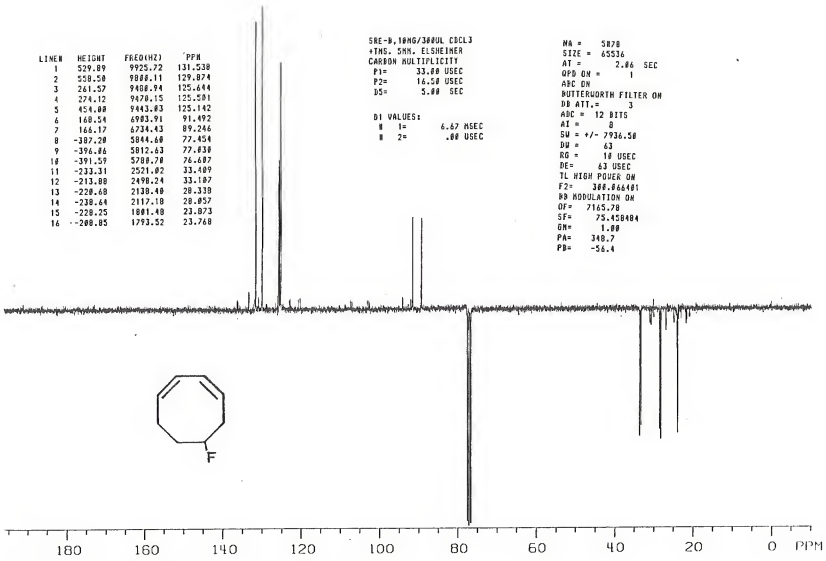


Figure B-28. ^{13}C NMR Spectrum of 44.

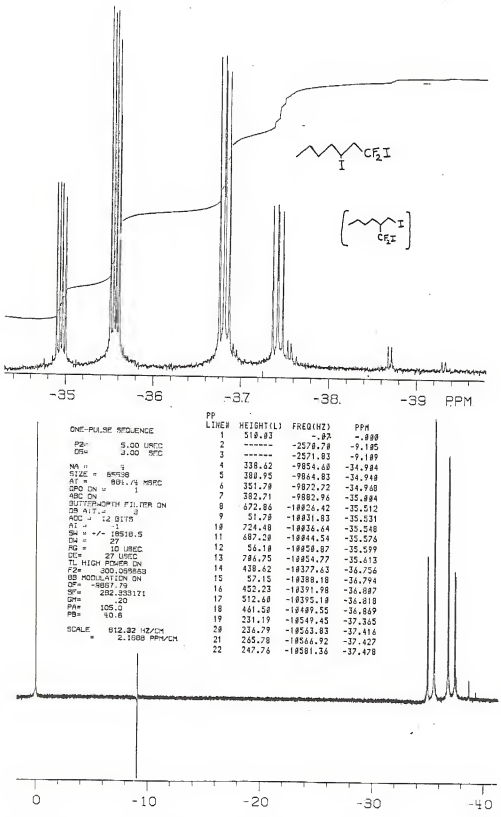


Figure B-29. ^{19}F NMR Spectrum of 61.

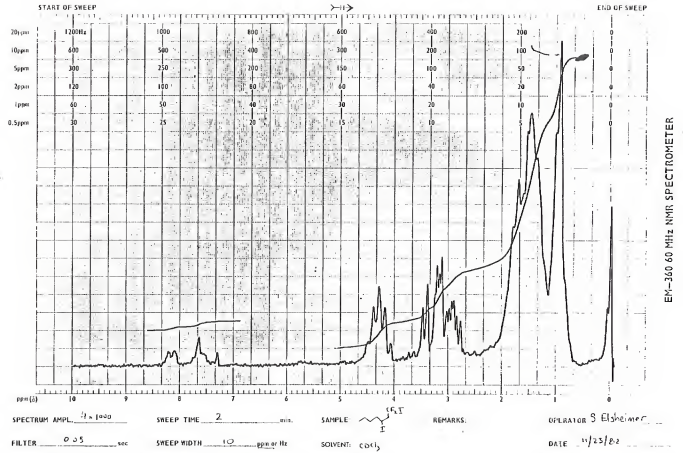


Figure B-30. ^{1}H NMR Spectrum of 61.

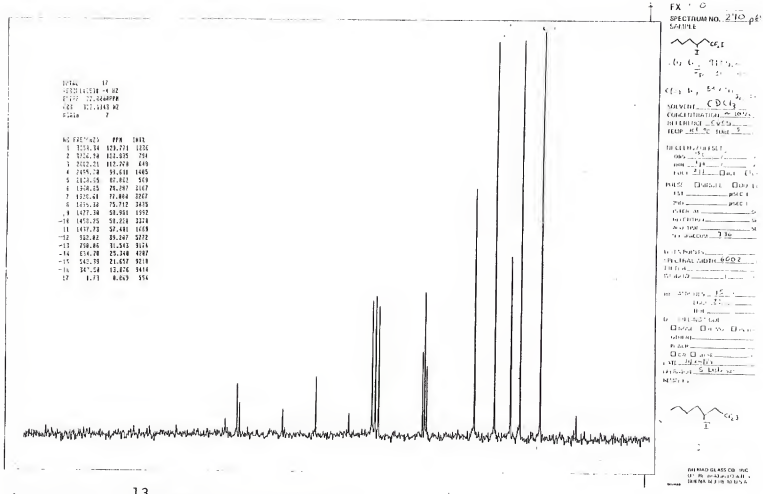


Figure B-31. ^{13}C NMR Spectrum of 61.

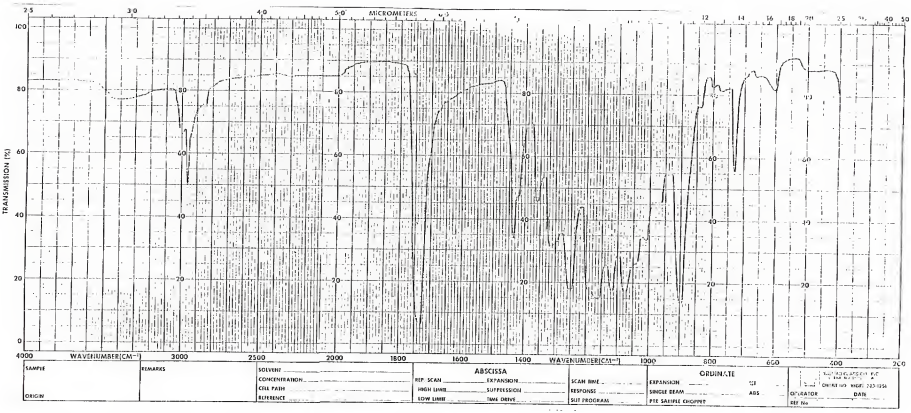


Figure B-32. IR Spectrum of 63.

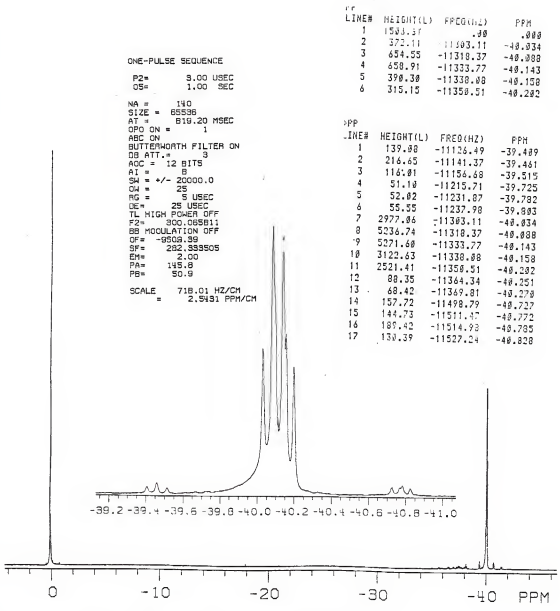


Figure B-33. ^{19}F NMR Spectrum of 63.

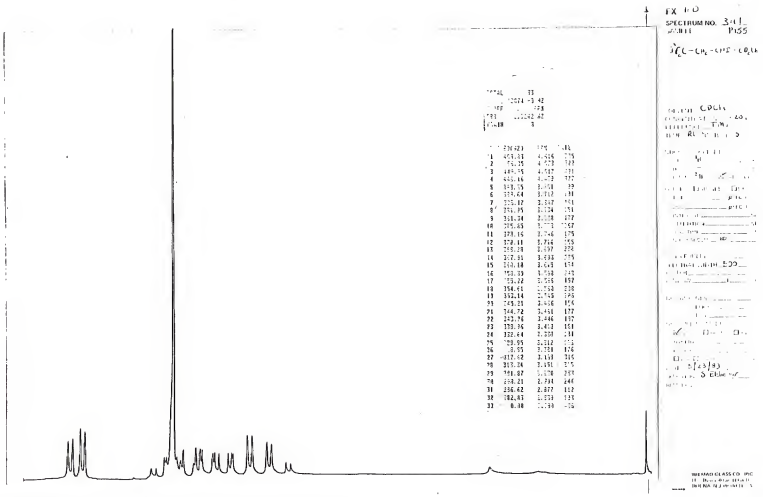


Figure B-34. ^{1}H NMR Spectrum of 63.

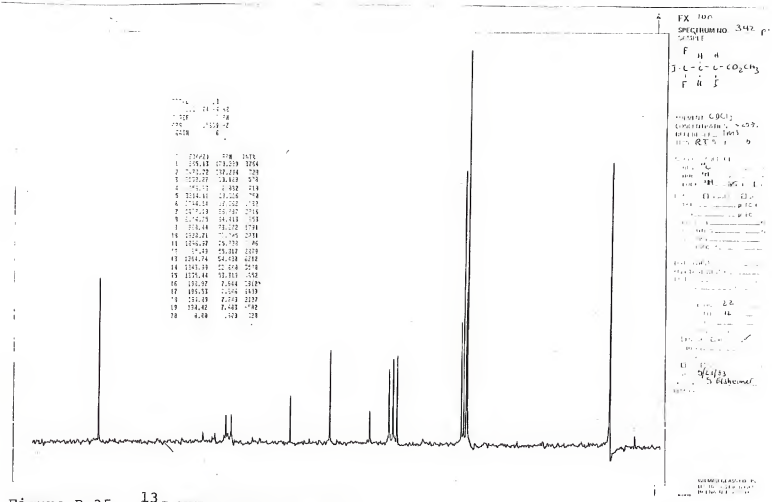


Figure B-35. ^{13}C NMR Spectrum of 63.

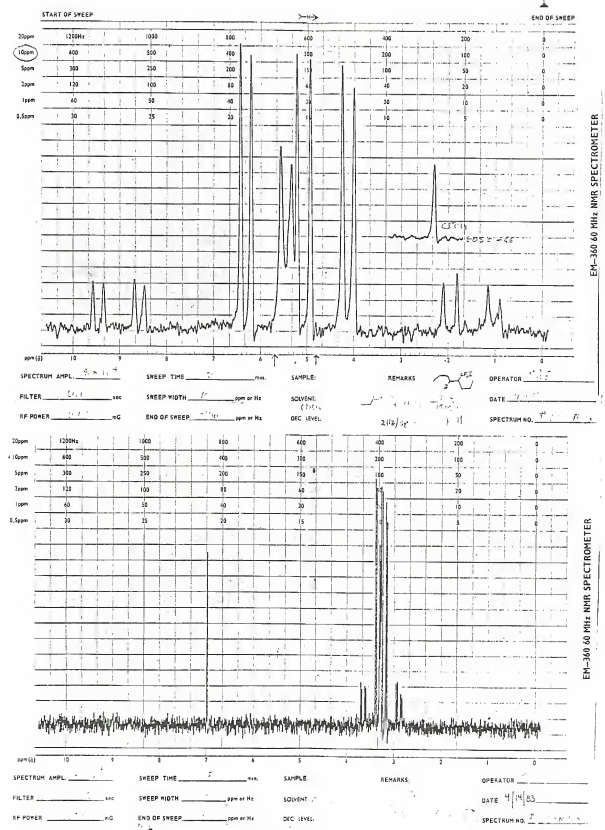


Figure B-36. ^{1}H NMR Spectrum of 65.

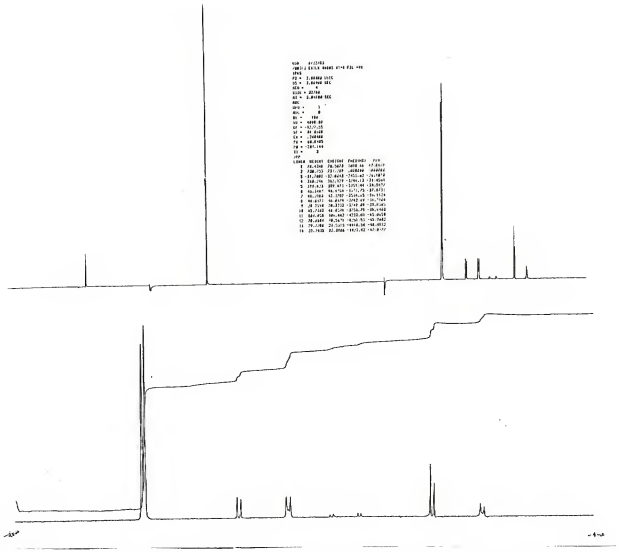


Figure B-37. ^{19}F NMR Spectrum of Reaction Mixture Containing 67 and 68.

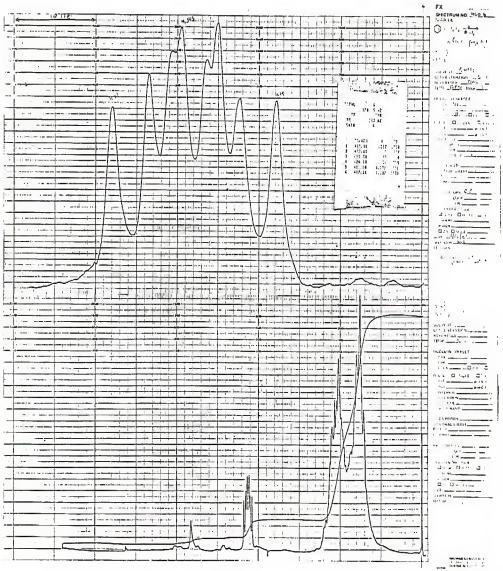


Figure B-38. ^{1}H NMR Spectrum of 67.

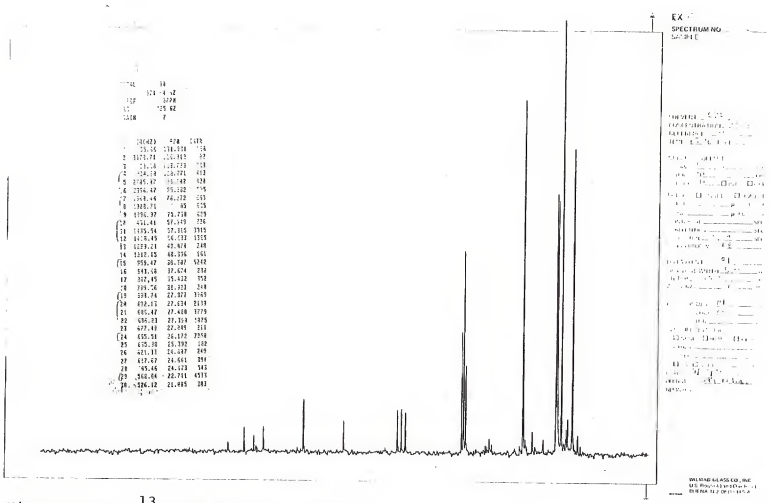


Figure B-39. ^{13}C NMR Spectrum of 67.

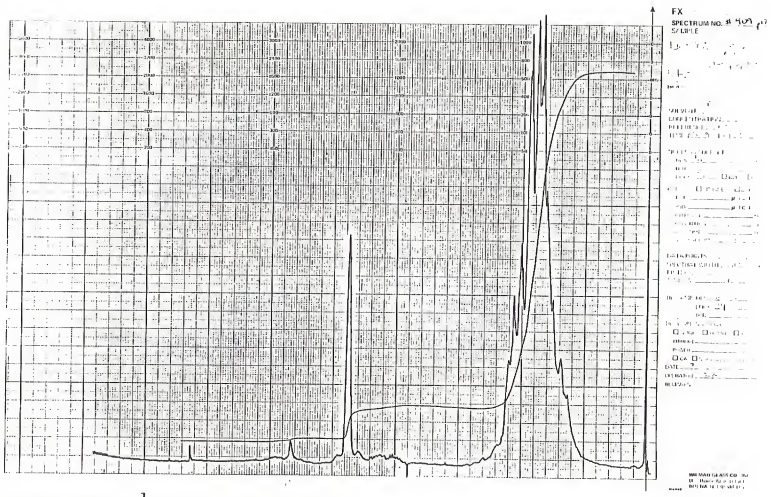


Figure B-40. ^{1}H NMR Spectrum of 68.

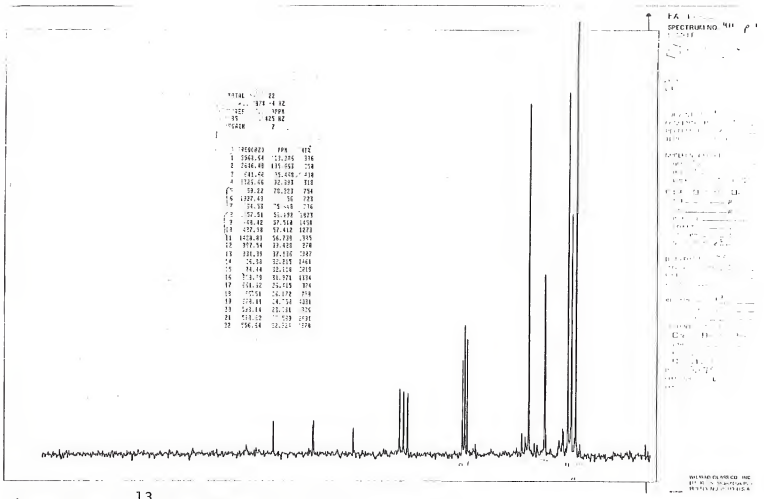


Figure B-41. ^{13}C NMR Spectrum of 41.

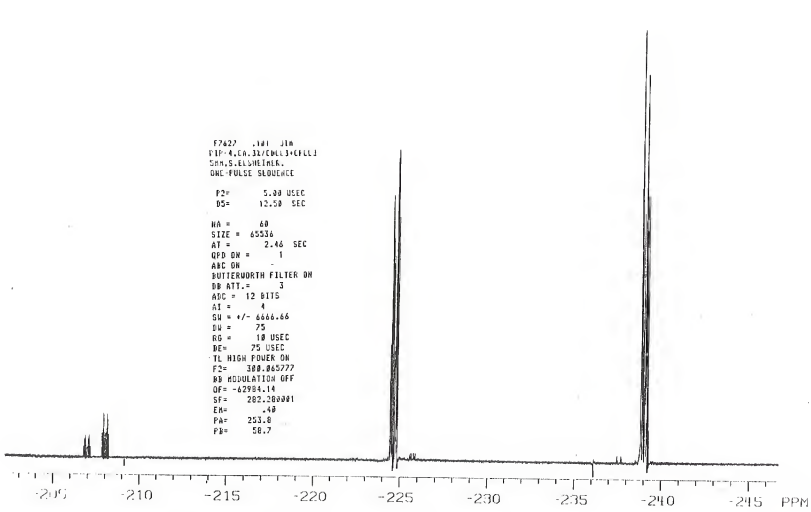


Figure B-42. ^{19}F NMR Spectrum of a Mixture of 72, 73, 74, and 75. (Note: See also expansions Figure B-43.)

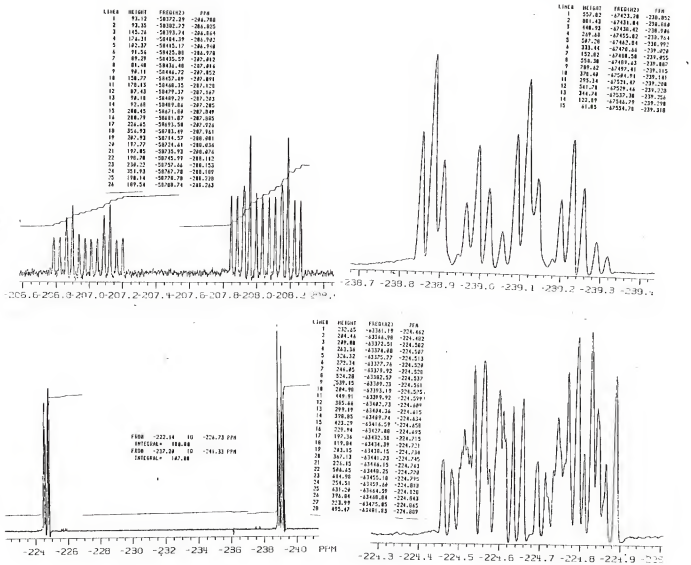


Figure B-43. Expansions of the ^{19}F NMR Spectrum of a Mixture of 72, 73, 74, and 75.

REFERENCES

1. B. E. Smart, "The Chemistry of Functional Groups, Supplement D", S. Patai, Z. Rappaport, Eds., John Wiley & Sons, Ltd., Chichester, 1983, Part 2, Ch 14: "Fluorocarbons".

2. B. E. Smart, "Molecular Structures and Energetics", J. F. Liebman, A. Greenberg, Eds., Verlag Chemie International, Inc., Deerfield Beach, in press. Ch 3: "Fluorinated Organic Molecules".

3. H. A. Bent, Chem. Rev., 1961, 61, 275.

4. M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, A. G. Maki, J. Phys. Chem. Ref. Data, 1979, 8, 619.

5. G. A. Olah and Y. K. Mo, Adv. in Fluorine Chem., 1973, 7, 69.

6. L. Pauling, "Nature of the Chemical Bond", 3rd ed., Cornell Univ. Press, Ithaca, N.Y., 1960, 314-316.

7. D. F. McMillen, D. M. Golden, Ann. Rev. Phys. Chem., 1982, 33, 493.

8. J. M. Pickard, A. S. Rodgers, Int. J. Chemical Kinetics, 1983, 15, 569.

9. K. W. Egger, A. T. Cocks, Helv. Chim. Acta, 1973, 56, 1516.

10. N. C. Baird, Can. J. Chem., 1983, 61, 1567.

11. L. Radom, W. J. Hehre, J. A. Pople, J. Am. Chem. Soc., 1971, 93, 289.

12. H. Förster, F. Vögtle, Angew. Chem. Int. Ed. Eng., 1977, 16, 429.

13. P. D. Bartlett, R. C. Wheland, J. Am. Chem. Soc., 1972, 94, 2145.

14. W. R. Dolbier, Jr., K. S. Medinger, A. Greenberg, J. F. Liebman, Tetrahedron, 1982, 38, 2415.

15. J. D. Dill, A. Greenberg, J. F. Liebman, J. Am. Chem. Soc., 1979, 101, 6814.

16. J. Hine, "Structural Effects on Equilibria in Organic Chemistry", John Wiley & Sons, New York, 1975, 273.

17. A. J. Devaquet, R. E. Townshend, W. J. Hehre, J. Am. Chem. Soc., 1976, 98, 4068.

18. C. W. Bock, P. George, G. J. Mains, M. Trachtman, J. Chem. Soc. Perkin Trans. II, 1979, 814.

19. S. W. Benson, J. Chem. Ed., 1965, 42, 502.

20. J. M. Pickard, A. S. Rodgers, J. Am. Chem. Soc., 1979, 99, 695.

21. E-C. Wu, A. S. Rodgers, J. Am. Chem. Soc., 1976, 98, 6112.

22. W. R. Dolbier, Jr., Acct. Chem. Res., 1981, 14, 195, and references cited therein.

23. A. Greenberg, J. F. Liebman, "Strained Organic Molecules", Academic Press, New York, 1978, 1-55.

24. A. T. Perretta and V. W. Laurie, J. Chem. Phys., 1975, 62, 2469.

25. O. Bastiansen, F. N. Fritsch, K. Hedberg, Acta Crystal., 1964, 17, 583.

26. W. A. Bernett, J. Org. Chem., 1969, 34, 1772.

27. C. A. Deakyne, L. C. Allen, N. C. Craig, J. Am. Chem. Soc., 1977, 99, 3895.

28. W. R. Dolbier, Jr., S. F. Sellers, J. Am. Chem. Soc., 1982, 104, 2494.

29. W. R. Dolbier, Jr., S. F. Sellers, J. Org. Chem., 1982. 47, 1.

30. R. Hoffmann, Tet. Lett., 1970, 2907.

31. H. Günther, Tet. Lett., 1970, 5173.

32. D. Walsh, Trans. Faraday Soc., 1949, 45, 179.

33. T. Clark, G. W. Spitznagel, R. Klose, P.v.R. Schleyer, J. Am. Chem. Soc., 1984, 106, 4412.

34. J. J. Gajewski, J. Am. Chem. Soc., 1970, 92, 3688.

35. J. C. Gilbert, Tetrahedron, 1969, 25, 1459.

36. W.v.E. Doering, J. C. Gilbert, Tetrahedron Suppl., 1966, 7, 397.

37. M. C. Flowers, H. M. Frey, J. Chem. Soc., 1961, 5550.

38. W. R. Dolbier, Jr., S. F. Sellers, B. H. Al-Sader, S. R. Elsheimer, J. Am. Chem. Soc., 1981, 103, 715.

39. D. Seyferth, S. P. Hopper, J. Org. Chem., 1972, 37, 4070.

40. W. R. Dolbier, Jr., J. H. Alonso, J. Am. Chem. Soc., 1973, 95, 4421.

41. J. B. Lambert, L. G. Greifenstein, J. Am. Chem. Soc., 1974, 96, 5120.

42. Y. Kanazawa, J. D. Baldesweiler, N. C. Craig, J. Mol. Spectrosc., 1965, 16, 325.

43. D. R. James, G. H. Birnberg, L. A. Paquette, J. Am. Chem. Soc., 1974, 96, 7465.

44. W. R. Dolbier, Jr., C. R. Burkholder, Tet. Lett., 1983, 24, 1217.

45. R. J. Ellis, H. M. Frey, J. Chem. Soc., 1964, 5578.

46. D. S. Glass, R. S. Boikess, S. Winstein, Tet. Lett., 1966, 999.

47. H. M. Frey, R. K. Solly, Int. J. Chem. Kinetics, 1969, 1, 473.

48. J. Nishimura, J. Furukawa, J.C.S. Chem. Comm., 1971, 1375.

49. A. Greenberg, J. F. Liebman, W. R. Dolbier, Jr., K. S. Medinger, A. Skancke, Tetrahedron, 1983, 39, 1533.

50. W. Grimme, Chem. Ber., 1965, 98, 756.

51. W. J. Feast, J. B. Morland, J. Fluor. Chem., 1981, 18, 57.

52. J. Hine, R. Butterworth, P. B. Langford, J. Am. Chem. Soc., 1958, 80, 819.

53. I. McAlpine, H. Sutcliffe, J. Phys. Chem., 1969, 73, 3215.

54. I. McAlpine, H. Sutcliffe, Spectrochim. Acta, 1969, 25A, 1723.

55. W. Mahler, Inorg. Chem., 1963, 2, 230.

56. R. A. Mitsch, J. Heterocyclic Chem., 1964, 1, 233.

57. H. S. Kelsing, D. J. Burton, Tet. Lett., 1975, 3355.

58. G. A. Wheaton, D. J. Burton, J. Org. Chem., 1978, 2643.

59. R. E. McArthur, J. H. Simons, "Inorganic Synthesis", L. F. Audrieth, Ed., McGraw-Hill, New York, 1950, Vol. 3, 37.

60. H. Sorous, J. B. Hinkamp, J. Am. Chem. Soc., 1945, 67, 1642.

61. P. J. Kropp, N. J. Pienta, J. A. Sawyer, R. P. Polniaszeck, Tetrahedron, 1921, 37, 3229.

62. J. L. Hahnfeld, D. J. Burton, Tet. Lett.,1975, 1819.

63. J. T. Rawson, I. T. Harrison, J. Org. Chem., 1970, 35, 2057.

64. O. Repič and S. Vogt, Tet. Lett., 1982, 23, 2729.

65. P. Tarrant, A. M. Lovelace, J. Amer. Chem. Soc., 1954, 76, 3466.

66. A. Beverloo, M. C. Dieleman, P. Everkade, K. S. DeVries, B. M. Wepster, Rec. Trav. Chim., 1962, 81, 1033.

67. L. Kaplan, J. Am. Chem. Soc., 1967, 89, 1753.

68. W. F. Bailey, P. Gagnier, Tet. Lett., 1982, 23, 5123.

69. D. Wendisch, "Methoden der Organischen Chemie",George Theime Verlag, Stuttgart, 1971, Vol.4, pt. 3. and references cited therein.

70. D. J. Burton, J. L. Hahnfeld, Fluor. Chem. Rev., 1977, 8, 119.

71. C. F. Lane, G. W. Kramer, Aldrichimica Acta, 1977, 10, 11.

72. C. R. Noler, "Organic Syntheses, Collective Volume II" A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, 1943, p 184.

73. W. Carpenter, A. Haymaker, D. W. Moore, J. Org. Chem., 1966, 31, 789.

74. G. A. Wheaton, D. J. Burton, J. Fluor. Chem., 1977, 9, 25.

75. R. N. Keller, H. D. Wycoff, Inorg. Syn., 1946, 2, 1.

76. W. C. Still, M. Kahn, A. Mitra, J. Org. Chem., 1978, 43, 2923.

BIOGRAPHICAL SKETCH

Seth Elsheimer spent most of his early years in Florida's Hollywood/Fort Lauderdale area. He attended Broward Community College on a Math and Science Divisional Honors scholarship and graduated with highest honors from there in 1976 with an A.A. degree. In 1978, he received his B.S. degree in chemistry from Florida Atlantic University. In the fall of the same year, he began graduate studies at the University of Florida. Seth's academic honors include membership in Phi Theta Kappa and Phi Kappa Phi, and he has twice received the award for best student presentation in Organic/Bioorganic/Polymer Chemistry Division at the Florida meeting of the American Chemical Society (1981 and 1983).

Seth has been a long time lover of theatre and, after years of being a "closet Thespian," he made his stage debut in 1983. Within a year he appeared in several Gainesville theatres with roles in Fiddler on the Roof, A Funny Thing Happened on the Way to the Forum, The Unsinkable Molly Brown, A Christmas Carol, Li'l Abner, and Absurd Person Singular.

At the time of graduation from the University of Florida, Seth had accepted a postdoctoral research position at the University of California, San Diego.

Gainesville Sun, September 8, 1984.

Kevin Kolczynski/Sun staff photographer

Gas under glass

Seth Elsheimer checks a stirring apparatus made of glass in his UF laboratory. Elsheimer, a chemisty graduate student, was measuring the speed of a chemical reaction of gas.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William R. Dolbier, Jr.
Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William M. Jones
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Merle A. Battiste
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Hendrik J. Monkhorst
Professor of Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Assistant Professor of Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1984

Dean for Graduate Studies
and Research